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Monofunctional and Polyfunctional Phosphinimine Ligands and Their Transition Metal Complexes

by

Jin Li ©

A thesis

submitted to the Faculty of Graduate Studies and Research

in partial fulfillment of the requirements

for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta

Spring 1996

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Monofunctional and Polyfunctional Phosphinimine Ligands and Their Transition Metal Complexes** submitted by Jin Li in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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March 25, 1996

For my parents, brothers, and my wife, Zhongqi

Abstract

A series of mono- and polyfunctional nitrogen and/or phosphorus donor center containing derivatives of substituted cyclic organic compounds has been prepared. These new materials form neutral and cationic complexes of rhodium(I) in which the metal is coordinated *via* the nitrogen, phosphorus or π-electron donor sites.

Reactions of 1,3-dicyanotetrafluorobenzene with trimethylsilyl phosphinimines, $Me_3SiN{=}PR_3$, proceed through stepwise substitution on the fluoroaromatic to yield mono- and disubstituted derivatives of the form $4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}A\text{-}3\text{-}B$. The disubstituted derivatives ($A = B = N{=}PR_3$) and the monosubstituted derivatives $a,b\text{-}(CN)_2C_6F_3\text{-}1\text{-}A$, (a,b is 2,4, 2,5 or 3,4; and $A = N{=}PR_3$) readily react with $[Rh(cod)Cl]_2$ and $AgClO_4$ to yield cationic Rh(I) complexes in which the nitrile groups coordinate to the Rh center using either the lone pair on nitrogen (σ coordinated dimer structure, in which the CN stretching frequencies were increased) or the CN triple bond (π coordination, in which the CN stretching frequencies were substantially decreased).

A bifunctionally substituted ($A = B = N{=}P(Ph)_2CH_2PPh_2$) ligand has been prepared which forms either a dinuclear complex $[4,6\text{-}(CN)_2\text{-}C_6F_2\text{-}1,3\text{-}\{\overline{N{=}P(Ph)_2CH_2P(Ph)_2R}h(CO)Cl\}_2]$ or a mononuclear complex $[4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2\}_2Rh(CO)Cl]$. The structure of the latter has been deduced from the second-order ^{31}P NMR spectrum. The mononuclear complex can be converted to a dinuclear complex by reaction with another equivalent of either the same or a different metal precursor, and the dinuclear complex can be reverted to the mononuclear complex by reaction with an equivalent amount of ligand.

Reaction of halogenated 1,4-benzoquinones with either one or two equivalents of a trimethylsilyl phosphinimine gives the monosubstituted or disubstituted

respectively. The former are converted to differently disubstituted derivatives upon reaction with an equivalent amount of either a different trimethylsilyl phosphinimine or aniline. Each of these ligands forms Rh(I) complexes which contain either π-coordinated or {O, N} σ-coordinated phosphinimine substituted quinone derivatives.

Reaction of N-trimethylsilyl-3,5-dimethylpyrazole with cyanuric chloride gave mono-, di- and trisubstituted derivatives. The mono- and disubstituted derivatives react further with $Me_3SiN=PR_3$ or $Me_3SiN=P(Ph)_2CH_2PPh_2$ giving new multifunctional chelating ligands. The reaction of $Me_3SiN=PR_3$ with cyanuric chloride yielded a ligand which formed a four-membered cationic {N, N} ring complex with Rh(I) precursor.

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List of Abbreviations

cod	1,5-cyclooctadiene (C_8H_{12})
dppm	bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$)
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone ($C_8N_2O_2Cl_2$)
DMF	N, N-dimethylformamide
nbd	norbornadiene (C_7H_8)
py	pyridine (C_5H_5N)
tfb	tetrafluorobenzobicyclo[2,2,2]octatriene ($C_{12}H_6F_4$)
THF	tetrahydrofuran (C_4H_8O)
T	trimethylsilyl ($SiMe_3$)
TMS	tetramethylsilane
ppm	parts per million
ν	frequency (cm^{-1})
δ	chemical shift (ppm)

Chapter 1

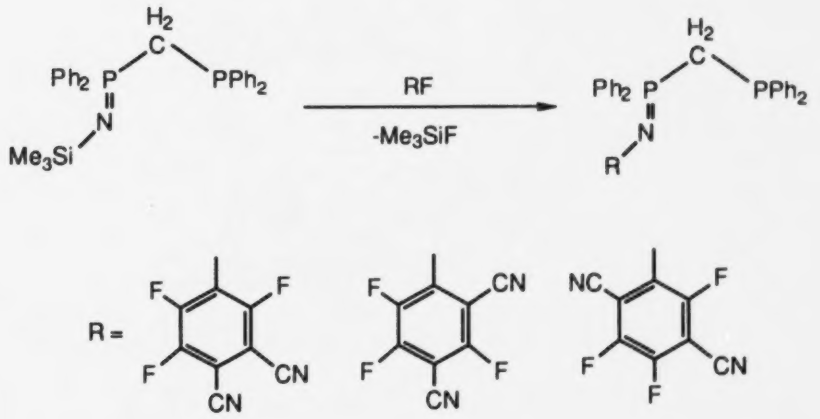
Introduction

1.1. Multifunctional Ligands Containing Phosphorus and Nitrogen Donors

Ligands with distinctly different heteroatom donors have received increased attention recently due to their capability of binding both the early and the late transition metals in both low and high oxidation states, and also due to the key role that such systems are likely to play in the development of useful catalysts and catalyst precursors for specific chemical transformations.[1-3]

Previous work in our group has revealed that silylated heterodifunctional phosphine-phosphinimines could be easily converted to cyanofluoroaromatic derivatives by substitution on the imine center, and that such species were effective ligands for binding both the early and the late transition metals (Scheme 1-1).[4,5]

Scheme 1-1:



In the previous work, only monosubstituted derivatives were obtained from the 1,2-, 1,3- and 1,4-dicyanofluoroaromatics.[5,6] As an extension, the disubstituted derivatives based on 1,3-dicyanotetrafluorobenzene have now been synthesized, and will be discussed in Chapter 2 of this thesis.

1.2. Transition Metal Complexes of Organonitrile Ligands

There has been considerable interest in metal-nitrile complexes since the 1960's.[7,8] Organonitrile ligands are important because the RCN group is isoelectronic with molecular nitrogen and carbon monoxide. However the nitrile ligands are relatively good σ-donors of moderate basic strength but are relatively poor π-acceptors from transition metals. As a result, organonitrile complexes contain weakly bound, labile ligands, and so these complexes are often used as convenient synthetic precursors to access a wide variety of metal complexes and compounds.

Since 1970, when Green[9] first reported that the complex $[Rh(cod)(MeCN)_2]BF_4$ catalyses both the hydrogenation of 1-hexene without concurrent isomerisation and the selective hydrogenation of 1,5-cyclooctadiene to cyclooctene, many analogous compounds have been prepared, using different diolefins and nitrile ligands (Table 1-1). Their hydrogenation catalysis behavior has also been studied.

Table 1-1. Complexes of types $[Rh(diolefin)L_2]^+A^-$ (L = nitrile ligand)

diolefin	L	A^-	Ref.
cod	MeCN	BF_4	9
cod	MeCN	ClO_4	10
cod	PhCN	ClO_4	10
cod	benzylnitrile	ClO_4	10
cod	*o*-tolunitrile	ClO_4	10

Table 1-1. continued

diolefin	L	A^-	Ref.
cod	malononitrile	ClO_4	10
cod	phthalonitrile	ClO_4	10
tfb	MeCN	ClO_4	11
tfb	PhCN	ClO_4	11
nbd	*o*-chlorobenzonitrile	ClO_4	12
nbd	*p*-methoxybenzonitrile	ClO_4	12
nbd	malononitrile	ClO_4	12
nbd	succinonitrile	ClO_4	12
nbd	phthalonitrile	ClO_4	12
tfb	4-CNPy	ClO_4	13
tfb	2-CNPy	ClO_4	13
cod	4-CNPy	ClO_4	13
cod	2-CNPy	ClO_4	13
nbd	4-CNPy	ClO_4	13

The range of ligands (L_2) has been extended to other nitrogen donor containing ligands and mixed nitrogen and phosphorus donor ligands, and complexes derived from many of these are also good hydrogenation catalysts. Examples include, (diolefin) = nbd, cod, tfb, L_2 = quinoline, isoquinoline, pyridine or 2-ethylpyridine, 4-NH_2py, 2-NH_2py, 4-NMe_2py, pyridine N-oxides, phosphines, phosphine oxides, or (L-L) = N,N,N',N'-tetramethylethylenediamine, 1,2-diphenylethylenediamine, 2,2'-bipyridine or 1,10-phenanthroline;[14-20] (diolefin) = 1,5-hexadiene, (L-L) = 2,2'-bipyridine, 1,10-phenanthroline and methyl substituted phenanthrolines;[21] (diolefin) = 1,5-hexadiene, (L-L) = 4,4'-Me_2Bipy, 4,7-Me_2Phen;[22] (diolefin) = cod, nbd, (L_2) = mono- or bidentate phosphine ligands.[23,24]

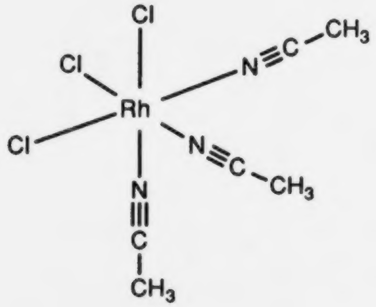
In principle, the RCN group may coordinate to metals in either of two ways: *via* end-on (σ) coordination using the lone pair of the nitrogen, or *via* a "side-on" coordination in which a π-orbital of the CN triple bond acts as the donor site.

1.2.1. Coordination Using the Lone Pair of the Nitrogen

1.2.1.1. Increase in ν_{CN} upon coordination

Most nitrile complexes show end-on coordination. In this case, the IR stretching frequencies arising from the CN triple bond may shift by small amounts to higher frequencies with respect to that of free nitrile ligands.[7]

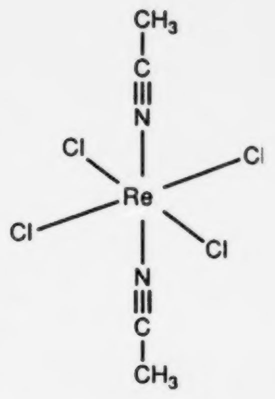
For example,[25] in the following metal complex the value for the nitrile stretching band is 2310 cm^{-1}, which is 55 cm^{-1} higher than that in the free ligand MeCN ($\nu_{CN} = 2255\ cm^{-1}$) (Figure 1-1).



$\nu_{CN} = 2310\ cm^{-1}$, $\Delta\nu = +55\ cm^{-1}$

Figure 1-1. Structure of *cis*-$Rh(NCCH_3)_3Cl_3$

In another example, Hamer[26] prepared *trans*-$ReCl_4(NCCH_3)_2$ ($\nu_{CN} = 2285\ cm^{-1}$), in which the corresponding band is 30 cm^{-1} greater than that in the free ligand (Figure 1-2).



$\nu_{CN} = 2285\ \text{cm}^{-1}$, $\Delta\nu = +30\ \text{cm}^{-1}$

Figure 1-2. Structure of *trans*-Re$(NCCH_3)_2Cl_4$

Uson[4] reported a series of nitrile complexes, $[Rh(cod)L_2]ClO_4$, (L = nitrile ligands) in which the values for ν_{CN} were greater by 20-50 cm^{-1} than the corresponding bands in the free ligands. For nitrile-transition metal complexes in which there is no significant (metal)π to (nitrile)π^* back-bonding, the range of increase in ν_{CN} upon coordination is generally 20-50 cm^{-1}. However, for the non-transition metal complexes the range is larger. For example, in the case of $SbF_5 \cdot NCCH_3$,[27] the change of ν_{CN} was +61 cm^{-1} and in the case of $X_3B \cdot NCCH_3$, (X=F, Cl, Br)[28,29] the increase of ν_{CN} was +100 cm^{-1}. The reason for the increase of the ν_{CN} upon coordination has not been fully elucidated.[8] It was only explained as an increase in the CN stretching force constant due to an increase in the strength of the CN σ-bond.[7,30,31] The reason for the increase in force constant and therefore stretching frequency has not been rationalized. This will be further discussed in Chapter 2 of this thesis.

1.2.1.2. Decrease in ν_{CN} upon coordination

Among the end-on coordinated nitrile transition metal complexes, some cases showed the ν_{CN} to be lower than those of the free nitriles, and it has been proposed that such a decrease of the ν_{CN} upon coordination is due to a decreased CN bond order caused by π-bonding between the metal d orbitals and the π* orbitals of the CN group. Among 10 nitrile complexes of *trans*-$Mo(N_2)(NCR)(dppe)_2$, the values for ν_{CN} decreased significantly, from -42 to -125 cm^{-1},[32] and among sixty nitrile complexes of types $Mo(CO)_2(PR_3)_2(NCR')_2$ and $Mo(CO)_2(PR_3)_3(NCR')$, the ν_{CN} shifts ranged from -102 to -10 cm^{-1}.[33,34] In the series of $CpMn(CO)_2(NCR)$, the values for ν_{CN} decreased from -11 to -43 cm^{-1}.[35,36] For the complexes of [*trans*-$M(X)(NCR)(L\text{-}L)_2$][anion], (M = group VIII metals), the values for ν_{CN} decreased from -4 to -121 cm^{-1}.[37-39]

1.2.2. Coordination *via* π-Orbital Electron Donation

Although less common than donation *via* the terminal nitrogen centers, side-on CN coordination compounds have been reported.[40-58] When π (or side-on) coordination occurs, it appears that the CN stretching frequency shifts substantially to lower frequencies as a result of the perturbation to the CN π-bond structure. However, only three structures have been fully elucidated using X-ray diffraction. One is the structure of (π-trifluoroacetonitrile)bis(triphenylphosphine)-platinum(0) (Figure 1-3).

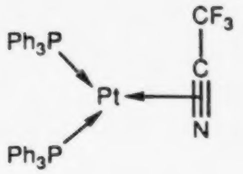

CF3
Ph3P
C
Pt
N
Ph3P

Figure 1-3. Structure of (π-F_3CCN)Pt(0)(PPh_3)$_2$

Even though the results of the complete X-ray study have not been published, the planar arrangement shown above for the platinum complex has been disclosed.[41] The IR spectrum showed a strong band at 1734 cm^{-1} which was assigned to the ν_{CN} stretching frequency. The shift of the ν_{CN} is -537 cm^{-1} compared with the band for the free ligand (F_3CCN is 2271 cm^{-1}).

The second CN π-bonded crystal structure is cyanamide compound, $[Ni(CO)(NCNC_5H_{10})]_3$, which shows that the terminal NC bond is "side-on" to the nickel centers (Figure 1-4).[48]

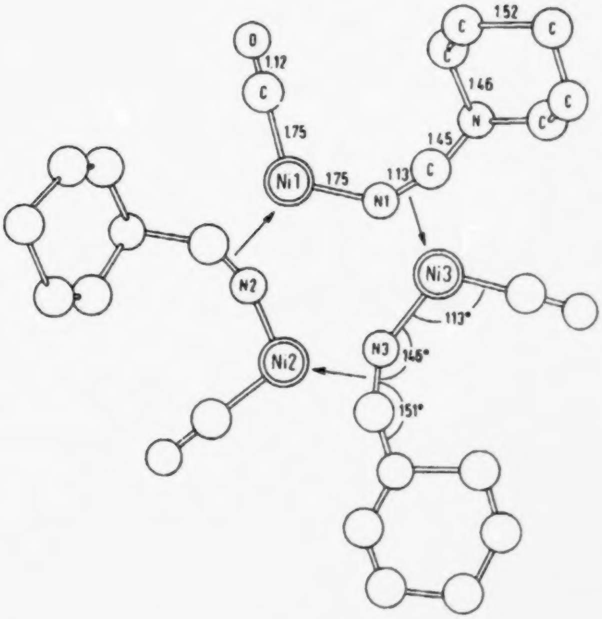
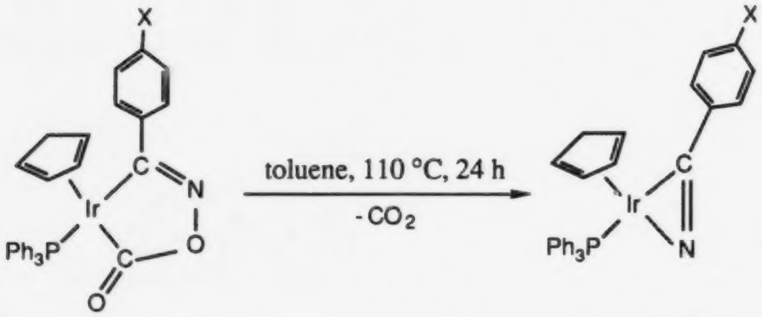

O
1.12
C
1.75
Ni1
1.75
N1
1.13
C
1.45
N
1.46
C
1.52
C
C
C
C
C
N2
Ni3
113°
N3
146°
Ni2
151°

Figure 1-4. Crystal Structure of $[Ni(CO)(NCNC_5H_{10})]_3$.

In this trimeric structure each Ni is linked by a σ bond to a cyano-N. At the same time, this CN ligand is π coordinated through the cyano triple bond to another metal. The C and N atoms of the CN groups are equidistant from the Ni atom (1.99 Å) to which they are π-bonded.

The third CN π-bonded crystal structure is reported by Hawthorne and coworkers.[57] The product was obtained from thermolysis of the metallacycle compound (Equation 1-1). The structure is shown in Figure 1-5.

Equation 1-1:



X = F, Cl

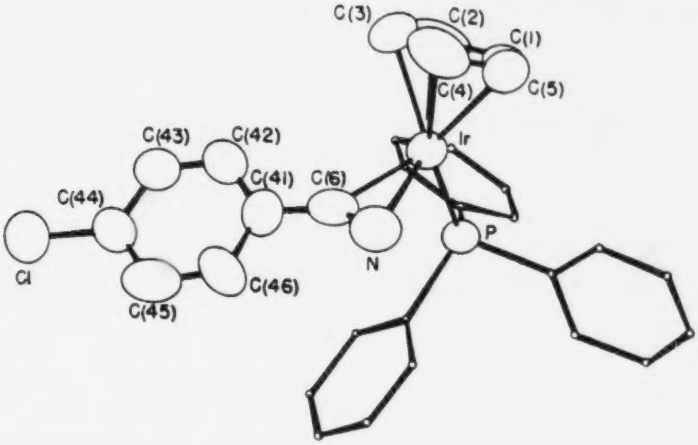


Figure 1-5. ORTEP drawing of [$(C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCC_6H_4Cl)$]. Hydrogen atoms have been omitted for clarity, and phenyl groups are depicted schematically.

In the structure shown in Figure 1-5, the C(6)-N bond length is 1.23(3) Å which is longer than that shown in Figure 1-4, (1.13Å). The *p*-chlorophenyl group attached to C(6) bent away from the metal center. This is because the hybridization of C(6) has been changed from sp to sp^2. The stretching frequencies of the two complexes shown in Equation 1-1 are 1756 and 1758 cm^{-1} respectively, a decrease of 468 and 472 cm^{-1} from the corresponding free nitriles.

Several other complexes have been prepared for which π-coordinated nitrile groups have been proposed (Table 1-2).

Table 1-2. Complexes proposed to have π coordinated nitrile groups.

Complexes	ν_{CN} (cm^{-1})	$\Delta\nu_{CN}$ (cm^{-1})	Ref.
$(F_3CCN)bis(Ph_3P)Pt(0)$	1374	-537	41
$[Ni(CO)(NCNC_5H_{10})]_3$	1988	-227	48
$[Ni(CO)(NCNMe_2)]_3$	2008	-204	42
$[(C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCC_6H_4F)]$	1756	-468	57
$[(C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCC_6H_4Cl)]$	1758	-472	57
$Cp_2Mo(NCR)$			
R = Me	1761	-494	55
$R = CF_3$	1745	-526	55
$R = C_6H_5$	1755	-489	55
$Co[P(OEt)_3]_3(NCR)$			
R = Me	1790	-465	56
$R = C_6H_5$	1755	-489	56
$(PPh_3)_4Ru(NCCH_3)\cdot CH_3CN$	1910	-344	52
$[(L_2MePt)_2 4\text{-}NCC_6F_4C(OEt)NH]^{2+}$	2141	-113	45
$L = PPhMe_2$			
$Cd(NCCH_2CN)_2Cl_2$	2200	-75	40
$[Mn(CO)[C_2H_5OC(O)CN]_2]_2$	2120	-140	44
$Fe(CO)[C_2H_5O(CO)CN]_3$	2120	-140	44
$[(PR_3)_3Co(NCR')]_3$			
$R = n\text{-}C_8H_{17}, R' = C_6H_5$	2130	-114	49
$R = n\text{-}C_8H_{17}, R' = CH_3$	2110	-156	49
$R = n\text{-}C_4H_9, R' = C_6H_5$	2120	-124	49
$R = C_6H_5, R' = C_6H_5$	2100	-144	49

Table 1-2. continued

Complexes	ν_{CN} (cm^{-1})	$\Delta\nu_{CN}$ (cm^{-1})	Ref.
$[M(CO)_3(Et_2NCH_2CN)]_2$			
M = Cr	2118	-102	47
M = Mo	2110	-110	47
M = W	2120	-100	47
$Fe(CO)_3(Et_2NCH_2CN)$	2110	-110	47
$[Mn(CO)_2(Et_2NCH_2CN)]_3$	2145/ 2120	-75/ -100	47
$[Cr(CO)_3(Et_2NCH_2CN)]^-$	2110	-110	47

The overall average of the above ν_{CN} change upon π-coordination of the CN group to transition metals is around -247 cm^{-1}.

1.2.3. Non-coordinated CN Groups

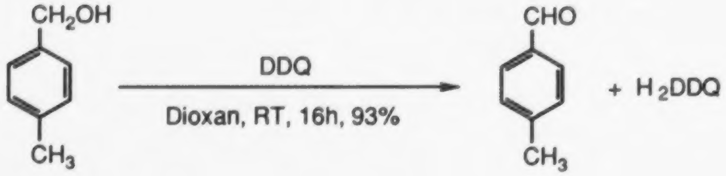
The CN stretching frequencies of the remote, uncoordinated nitrile group have been observed to shift upon coordination of other donor sites of the ligand, to either higher or lower frequencies. For example, the ν_{CN} in dichlorobis(3-cyanopyridine)palladium(II) is 8 cm^{-1} higher than in the free ligand.[54,59] In the analogous complex of 4-cyanopyridine, a decrease of 20 cm^{-1} was observed for the corresponding ligand.[59] In the complex $[Ru(NH_3)_5 1,3\text{-}C_6H_4(CN)_2]^{2+}$, ν_{CN} was found to be 3 cm^{-1} lower than in the free ligand.[60] In the complexes $[Re(CO)_3(PPh_2CH_2CH_2CN)_2X]$ (X=Cl, Br), the ν_{CN} associated with the free nitrile groups were observed at essentially the same frequencies observed for the free ligands.[61] Cotton et al. reported that in the complex $[Ni_4(CO)_6(P(C_2H_4CN)_3)_4]$, in which the nitrile groups are uncoordinated, the ν_{CN} did not shift upon coordination through only the phosphorus donor.[62,63]

1.3. Benzoquinone Derivatives and Their Transition Metal Complexes

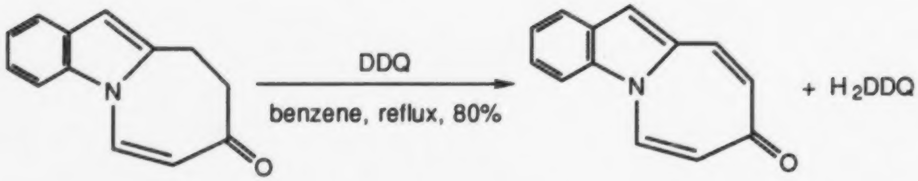
1.3.1. Importance of Quinone Derivatives

It is well known that quinone and hydroquinone provide a reversible redox system of considerable importance.[64] Quinone molecules play important roles both in synthetic chemistry and in biochemistry. In synthetic chemistry, quinones are usually used as oxidants and dehydrogenating agents (Equations 1-2, 1-3).[64,65]

Equation 1-2:


CH₂OH
CH₃
DDQ
Dioxan, RT, 16h, 93%
CHO
CH₃
+ H₂DDQ

Equation 1-3:


N
O
DDQ
benzene, reflux, 80%
N
O
+ H₂DDQ

In organometallic chemistry, benzoquinone is a convenient oxidant for conversion of a metallocene into the corresponding metallocinium ion in very high yield (Equation 1-4).[66,67]

Equation 1-4:

$$Cp_2M + DDQ \longrightarrow Cp_2M^+ \ DDQ^-$$

M = Fe or Co

In biochemistry, Vitamin E (Figure 1-6) and Vitamin K (Figure 1-7) are quinone derivatives.

Vitamin E:

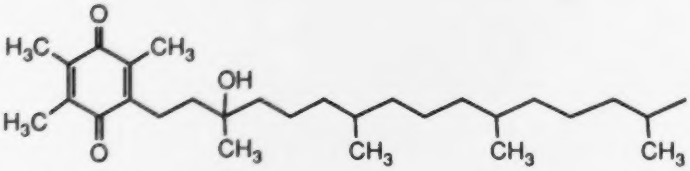


Figure 1-6. Structure of Vitamin E

Vitamin K:

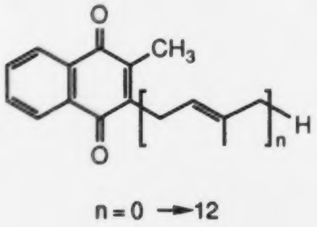


Figure 1-7. Structure of Vitamin K

The quinone based redox system constitutes one of the elements of the electron transport chain found in both photosynthesis and in respiration.[64] It is also reported that iron-quinone complexes serve as efficient electron carriers in mitochondria and in bacterial photosynthesis systems.[68,69]

Many quinone derivatives are useful dyes and pigments. The most frequently used quinone dyes are anthraquinone derivatives (Figure 1-8).[70]

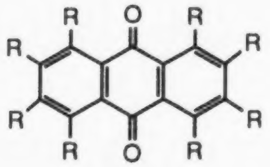
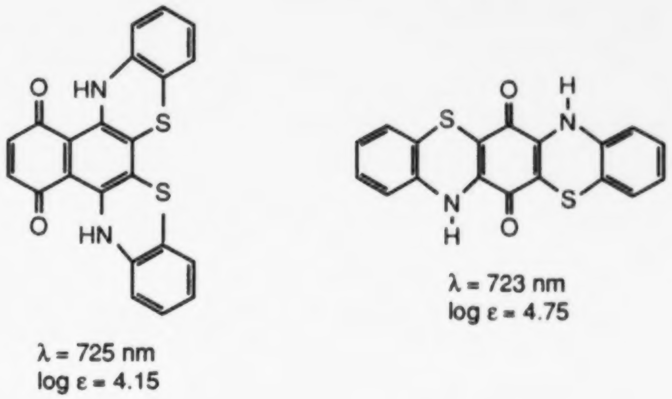


Figure 1-8. Structure of Substituted Anthraquinone

The substituents R can be variously H, alkyl, aryl, NH_2, NHR, halogen, SO_3Na, etc., and many established commercial applications are known. Some of the anthraquinone and naphthaquinone derivatives absorb light above 700 nm. Some benzoquinone derivatives are also near IR absorbers (Figure 1-9).[71,72]



λ = 725 nm
log ε = 4.15

λ = 723 nm
log ε = 4.75

Figure 1-9. Structures of Near IR absorbers of Naphthroquinone and Benzoquinone Derivatives

These near IR absorbers have very useful applications. For example, some anthraquinone and naphthoquinone derivatives are used as laser filters.[73] Compared with anthraquinone and naphthoquinone derivatives, the use of benzoquinone derivatives as dyes and pigments has been less extensively studied. Quinone dyes based on tetrachloro-1,4-benzoquinone are the subject of a review.[74] One of the earliest commercialized benzoquinone dyes is 2,5-bis(*p*-chloroanilino)-1,4-benzoquinone, which was commercially available in 1910 (Figure 1-10).[75]

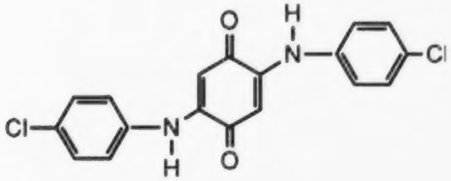


Figure 1-10. Structure of 2,5-bis(*p*-chlorophenylamino)-*p*-benzoquinone

The following benzoquinone nitro dye is brown-colored, and has the very valuable property of deep penetration into leather during the dyeing process (Figure 1-11).[70]

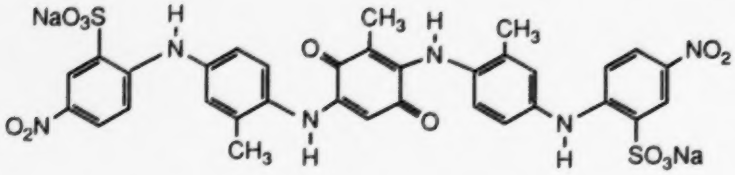


Figure 1-11. Structure of a benzoquinone Nitro Dye

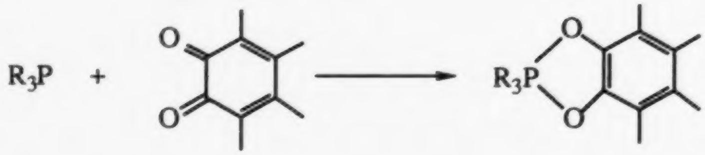
1.3.2. Organophosphorus Derivatives of Benzoquinones

Oxidative phosphorylation plays a role in energy transfer schemes in biological processes. The study of quinol phosphates shows potential for improving our understanding of the energy transduction in biological mechanisms.[76] However, there has been relatively little attention to the area; there exists one literature review surveying the reactions of phosphorus compounds with quinones.[77]

1.3.2.1. Reactions of tricoordinate phosphine with quinones

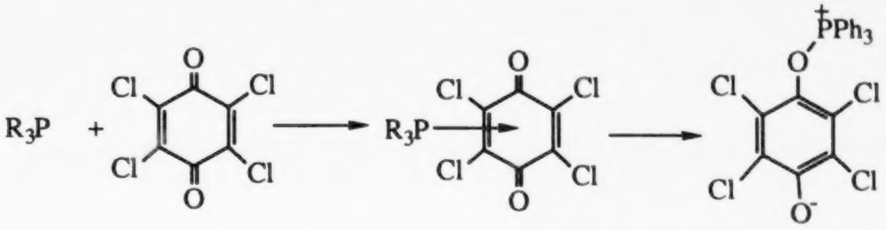
o-Quinones react with tricoordinate phosphines to form adducts which possess a cyclic phosphorane structure (Equation 1-5).[77]

Equation 1-5:



In contrast, *p*-quinones react with tricoordinate phosphines to form a variety of different products, the structure of which depends on the nature of R and substituents on the quinones. For example, reaction of triphenylphosphine with chloranil gives a product, which is formed as a result of the oxidation by the quinone of phosphine in the phosphine-quinone charge-transfer complexes (Equation 1-6).[78]

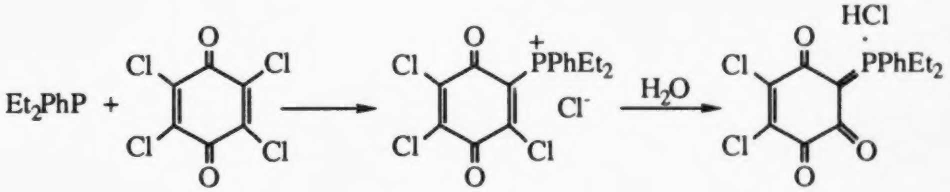
Equation 1-6:



R3P
+
Cl
O
R3P
+PPh3
O-

In contrast, diethylphenylphosphine reacts with chloranil to form a phosphorus-containing dipolar product, which in turn forms a new type of stable phosphorus ylide upon reaction with water (Equation 1-7).[79]

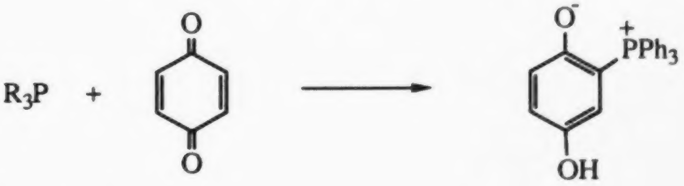
Equation 1-7:



Et2PhP +
Cl
O
+PPhEt2
Cl-
H2O
HCl
PPhEt2

The reaction of triphenylphosphine with *p*-benzoquinone gives the phosphobetaine (Equation 1-8).[78,80]

Equation 1-8:



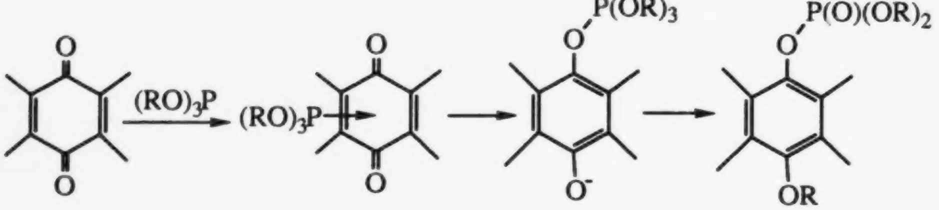
R3P
+
O
O-
+PPh3
OH

This reaction has been used to obtain a large series of quaternary phosphonium salts used to promote the interaction of vicinal epoxides with phenols in order to obtain polymer films.[78]

1.3.2.2. Reactions of phosphites with quinones

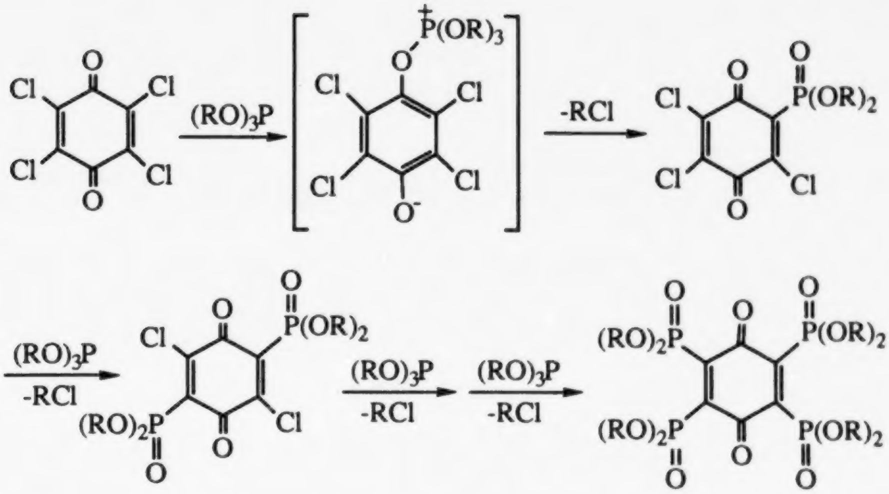
Phosphites react with *p*-benzoquinones to give in most cases stable aromatic phosphates (Equation 1-9).[79,81]

Equation 1-9:



If the phosphites have bulky substitutents, the reactions sometimes give unexpected products. For example, the reactions of triisopropyl and triisobutyl phosphites with chloranil proceed *via* the substitution of the chlorine atoms of chloranil by phosphoryl groups as a result of the intramolecular Arbuzov reaction.[82] The more common addition to the quinone is not observed (Equation 1-10).

Equation 1-10:

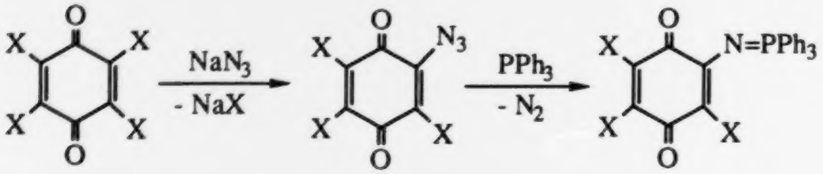


R = iso-Pr, iso-Bu.

1.3.2.3. Preparation of phosphinimine *p*-quinone derivatives

The first report of phosphinimine *p*-quinone compounds was in a US Patent.[83] The product was obtained from the reaction of azido-*para*-benzoquinone with trivalent phosphorus compounds and these materials were found to be useful as dyestuffs, as the active components of insecticides and as intermediates for synthesis of other compounds. However, no chemical and physical data were reported for these materials (Equation 1-11).

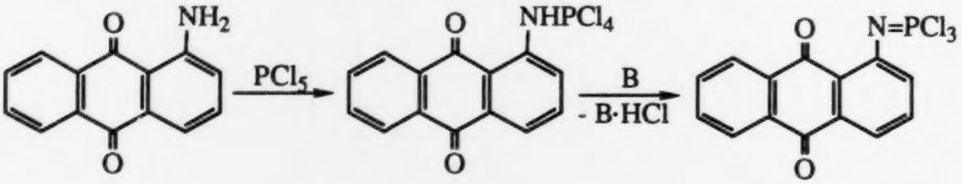
Equation 1-11:



X = halogen

A related example[84] of a phosphinimine on a quinone arises from the interaction of phosphorus pentachloride with 1-amino-anthraquinone, which yields the N-tetrachlorophosphoranyl-1-amino-anthraquinone. This product is converted into trichlorophosphazoanthraquinone by treatment with tertiary bases (Equation 1-12; B = Base).

Equation 1-12:



1.3.3. *o*-Benzoquinone Transition Metal Complexes

The chelating ability of *o*-benzoquinones has enabled formation of a large number of stable transition-metal compounds which have been extensively studied.[85-87] One example is [Pd(PPh$_3$)$_2$(*o*-Cl$_4$C$_6$O$_2$)], which has been structurally characterized (Figure 1-12).[88]

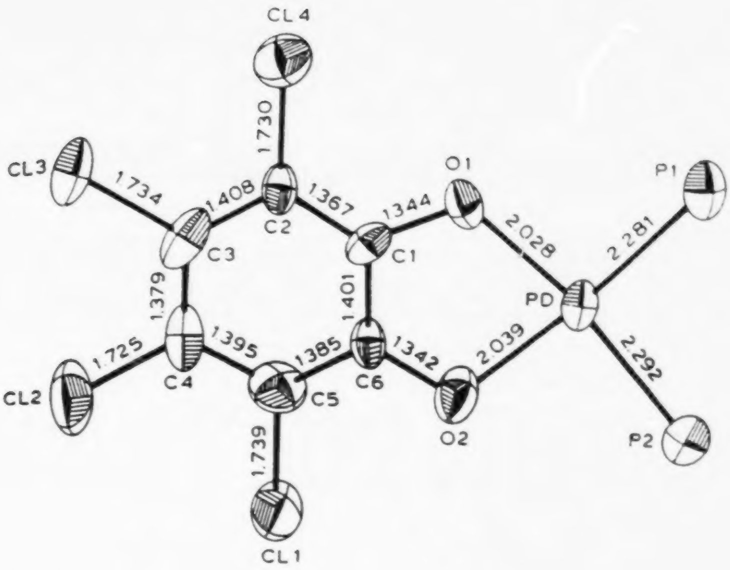
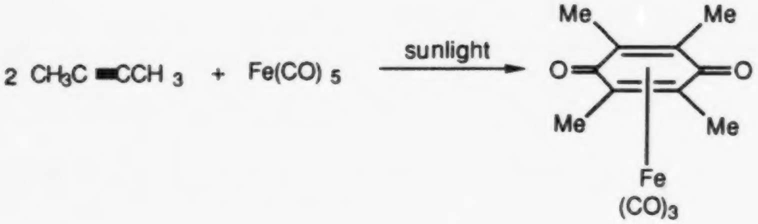

CL 4
1.730
CL3
1.734
1.408
C2
1.367
C1
1.344
O1
2.028
P1
2.281
C3
1.379
1.401
PD
CL2
1.725
C4
1.395
C5
1.385
C6
1.342
2.039
O2
2.292
P2
1.739
CL 1

Figure 1-12. Structure of $Pd(PPh_3)_2(o\text{-}Cl_4C_6O_2)$.

1.3.4. π-Coordinated *p*-Benzoquinone Transition Metal Complexes

Compared with the *o*-benzoquinone metal complexes, much less is known about transition-metal coordination compounds of *p*-benzoquinones which are not capable of forming chelates. Most of the known *p*-benzoquinone metal complexes are π-coordinated. Probably the first example of a π-quinone metal complex was π-duroquinone-$Fe(CO)_3$. This was not obtained directly from the reaction of duroquinone with $Fe(CO)_5$, instead, it was obtained from a mixture of dimethylacetylene and $Fe(CO)_5$ exposed to sunlight (Equation 1-13).[89]

Equation 1-13:


2 CH3C≡CCH 3
+
Fe(CO) 5
sunlight
Me
Me
O
O
Me
Me
Fe
(CO)3

This initial work prompted synthesis of a series of π-coordinated quinone metal complexes from the direct reaction of quinones with metal precursors.[90-113] One representative example is the bis-duroquinone-Ni(0) complex which was obtained by refluxing duroquinone with $Ni(CO)_4$ (Figure 1-13).[91]

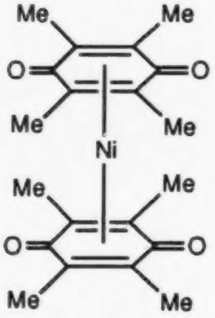

Me
Me
O
O
Me
Me
Ni
Me
Me
O
O
Me
Me

Figure 1-13. Structure of Bis-duraquinone Nickel(0)

This complex was subsequently obtained as a precursor for a second series of compounds in which one of the quinone ligands was replaced by an olefin. One such compound has been structurally characterized (Figure 1-14).[102]

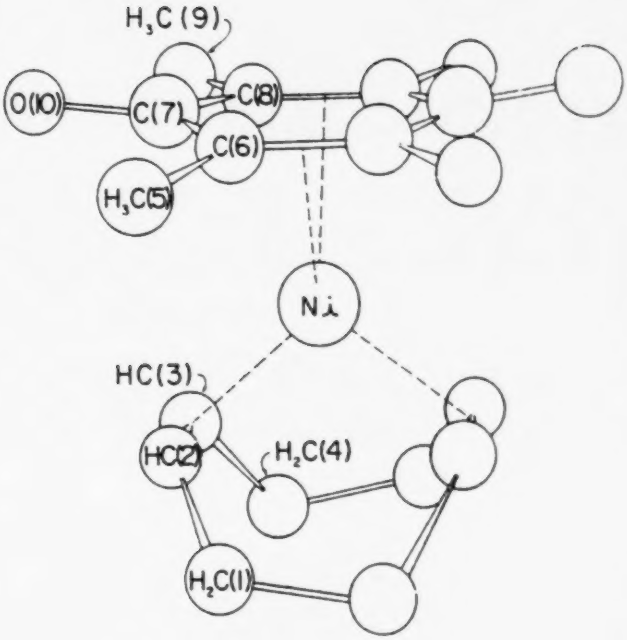


Figure 1-14. Structure of π-duroquinone-Ni(cod)

In this complex, the four methyl groups incline slightly towards the nickel atom, whilst the carbonyl oxygens are inclined in the opposite direction, the carbonyl bond making an angle of about 6° with the plane defined by the four other carbon atoms of the quinone ring.

Khandharova[106] and Aleksandrov[107] reported that in cyclopentadienyl-2,6-di-t-butyl-*p*-benzoquinonerhodium the quinone is even more strikingly distorted into a boat-shaped structure (Figure 1-15).

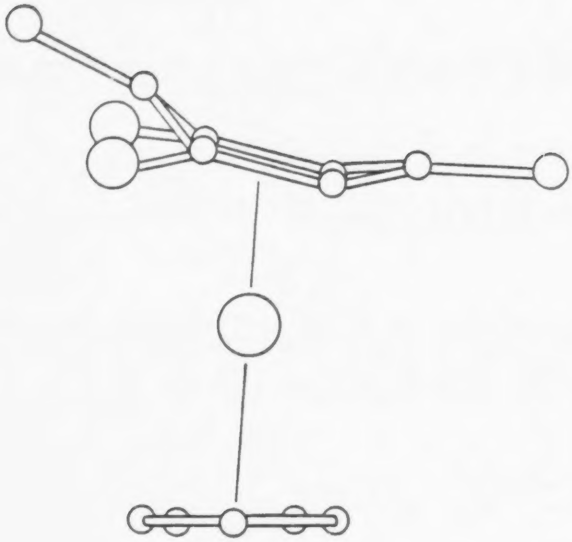
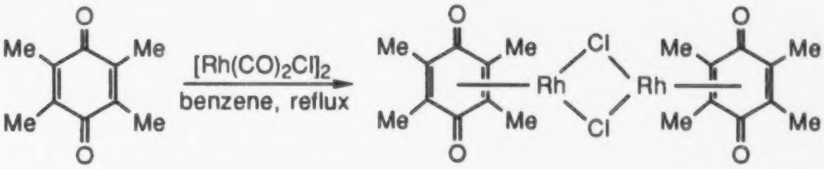


Figure 1-15. Structure of CpRh(2,6-t-butyl-*p*-benzoquinone)

Aleksandrov later pointed out that such distortion of the quinone fragment is probably general, rather than a consequence of specific steric effects occuring in this complex. Evaluation of the structure of CpRh(duroquinone), in which there is significant distortion of the quinone ligand, showed that steric interference effects are minimal.[108]

Duroquinone reacts with $[Rh(CO)_2Cl]_2$ in refluxing benzene to form a dimeric product (Equation 1-14).[103]

Equation 1-14:



Vitamin E has been reacted with $Ni(CO)_4$ and cycloocta-1,5-diene to form the first synthetic organometallic compound involving a natural product (Figure 1-16).[93]

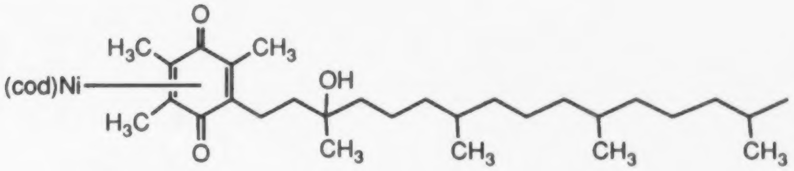
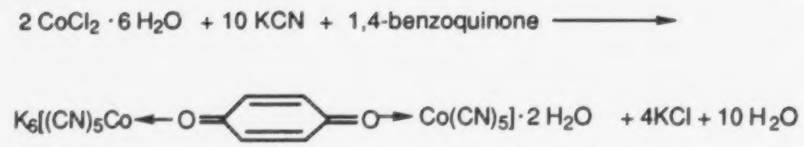


Figure 1-16. Structure of (cod)Ni(Vitamin E)

1.3.5. σ-Coordinated *p*-Benzoquinone Transition Metal Complexes

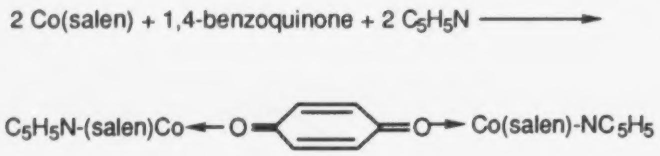
Although rare, a few examples are reported of *p*-benzoquinones which form σ-coordinated complexes in which the quinone functions as a bridge. One example is the pentacyanocobaltate anion which reacts with *p*-benzoquinone to form a dimeric product (Equation 1-15).[114]

Equation 1-15:


2 CoCl2 · 6 H2O + 10 KCN + 1,4-benzoquinone
K6[(CN)5Co ← O ═ ═ O → Co(CN)5] · 2 H2O + 4KCl + 10 H2O

Another example is provided by the reaction of 1,4-benzoquinone with Schiff's base metal complexes, such as N,N'-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), to form a dimeric product (Equation 1-16).[115]

Equation 1-16:


2 Co(salen) + 1,4-benzoquinone + 2 C5H5N
C5H5N-(salen)Co ← O ═ ═ O → Co(salen)-NC5H5

The scarcity of the stable σ-coordinated metal complexes of *p*-benzoquinones is principally due to the lability of simple *p*-benzoquinones which do not contain chelating substituents. Substituents on *p*-benzoquinones which contain donor sites could allow the possibility of forming chelated σ-coordinated *p*-benzoquinone metal complexes. For example, 2,5-dihydroxy-*p*-benzoquinone has two potential chelating sites, and this ligand has been used to form a series of σ-coordinated transition metal complexes.

Cr(III) complexes of 2,5-dihydroxy-1,4-benzoquinone and 2,5-dihydroxy-3,6-dichlorobenzoquinone are reported to be used under mild conditions (25 °C) as alcohol-oxidizing fuel cell catalysts, yielding acetaldehyde as the sole organic product.[116,117] If the ligands are combined with the metal salts in a 1:1 ratio, polymeric products are obtained, as was the case for 2,5-dihydroxy-3,6-dichlorobenzoquinone with Fe(II),[118] Co(II),[119-121] Ni(II),[119,120,122-124] Cu(II),[119,120,122,125] Sn(IV),[126] Pt(II),[127] and Pd(II),[127] and for 2,5-dihydroxy-1,4-benzoquinone with Fe(II),[118] Cu(II),[128] and Zn(II).[128]

Formation of polymeric products can be prevented by blocking the coordination positions with other polydentate ligands. In such cases dinuclear complexes are obtained instead. The Fe(III) quinone complex below,[118] contains both bridging and terminal dihydroxybenzoquinone ligands (Figure 1-17).

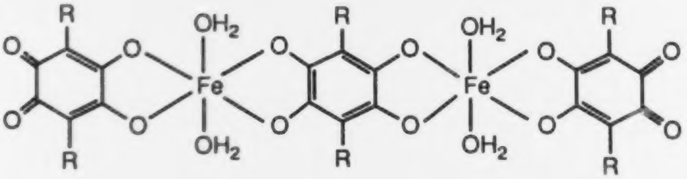


Figure 1-17. Structure of $(o\text{-}R_2C_6O_2)_3Fe_2(H_2O)_4$

Pierpont et al.[129] reported dinuclear complexes of $[Ni_2(tren)_2(CA)](BPh_4)_2$ and $[Cu_2(Me_5dien)_2(CA)](BPh_4)_2$, (CA = dianion of chloroanilic acid), both of which have been structurally characterized. Tinti et al.[130] reported dinuclear complexes of Cu(II) (Figure 1-18; R = H, Cl, Br, I and NO_2).

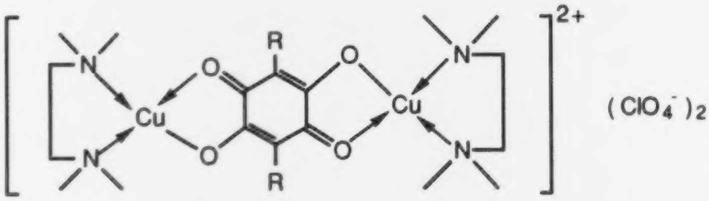


Figure 1-18. Structure of $[Cu_2(tmen)_2(CA)](ClO_4)_2$

The iodo derivative has been structurally characterized. Folgado et al.[131] also reported an X-ray crystal structure of $[Cu_2(terpy)_2(CA)](PF_6)_2$, (Figure 1-19; terpy = 2,2':6',2"-terpyridine).

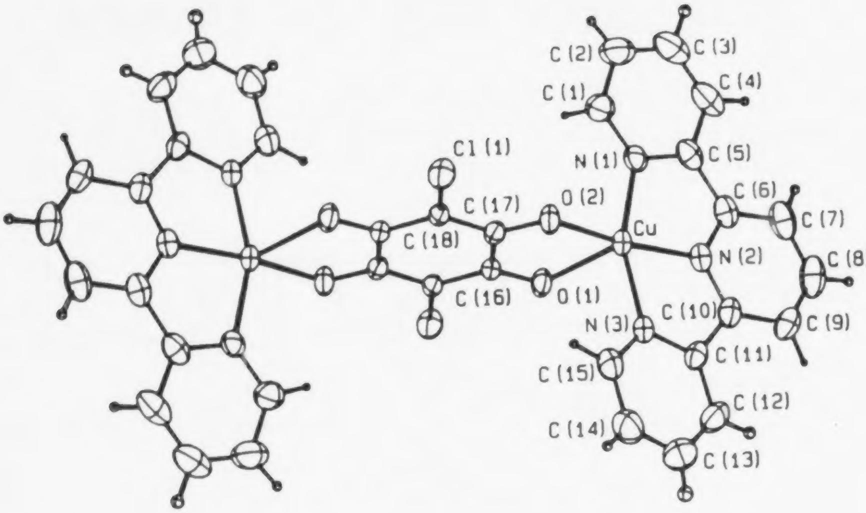

C (2)
C (3)
C (4)
C (1)
Cl (1)
N (1)
C (5)
C (6)
C (17)
O (2)
C (7)
Cu
C (18)
N (2)
C (8)
C (16)
O (1)
C (10)
C (9)
N (3)
C (11)
C (15)
C (12)
C (14)
C (13)

Figure 1-19. Crystal Structure of $[Cu_2(terpy)_2(CA)]^{2+}$

Recently, Calvo et al.[132] reported a crystal structure of a dinuclear complex of Rh(I) (Figure 1-20).

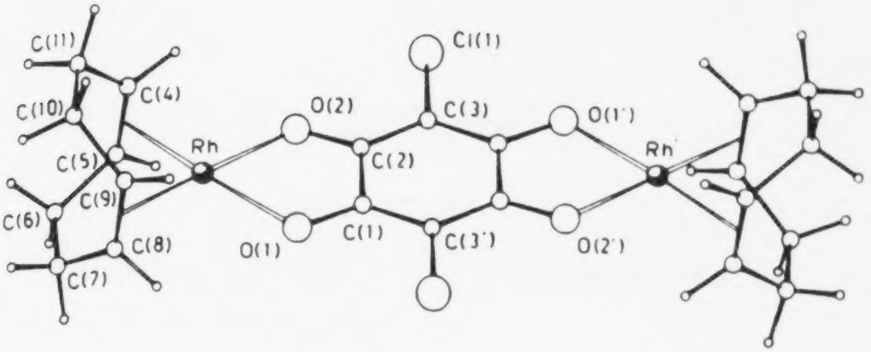
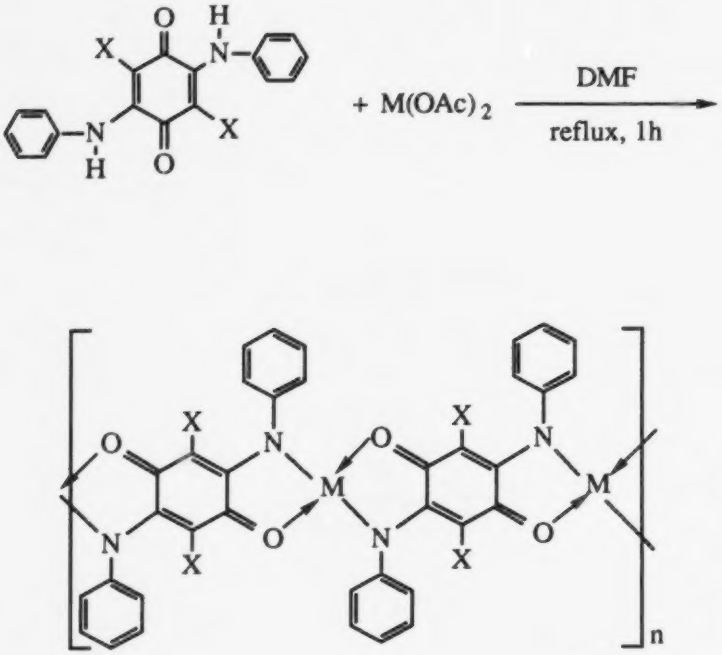


Figure 1-20. Crystal Structure of $[Rh_2(CA)(cod)_2]$

Although the above ligands, 2,5-dihydroxy-1,4-benzoquinone and 2,5-dihydroxy-3,6-dichlorobenzoquinone, are commercially available, few other substituted *p*-benzoquinones have been used as chelating ligands. One example is 2,5-bis(arylamino)-*p*-benzoquinone, obtained from the reaction of aniline with *p*-benzoquinone. The ligand reacted with compounds of the first row transition metals to form polymetallic materials (Equation 1-17).[133]

Equation 1-17:



X = Cl, Br
M = Co, Cu

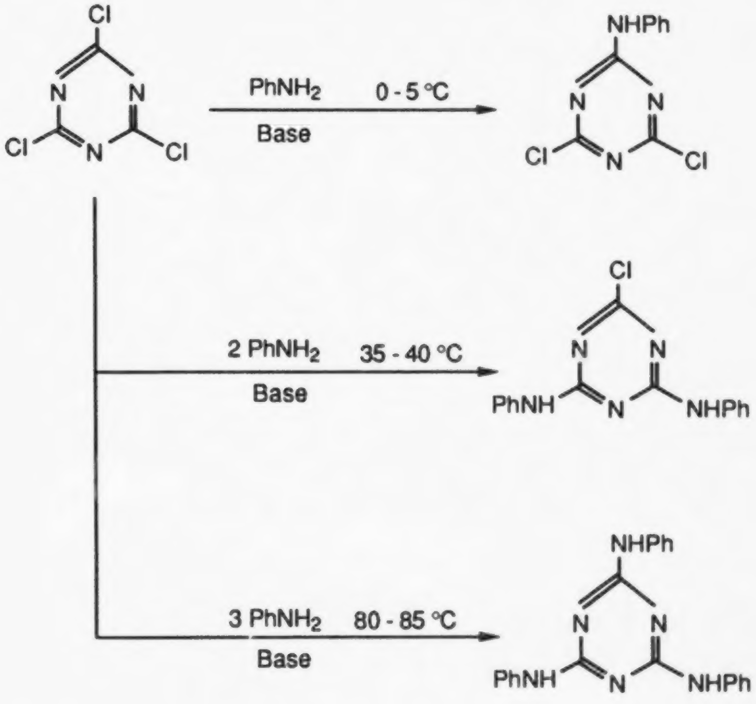
Unfortunately, the ligands themselves generally have very poor solubility and the resultant polychelates also are generally insoluble.

1.4. Properties of Cyanuric Chloride Derivatives

1.4.1. Roles of Cyanuric Chloride in Reactive Dyes

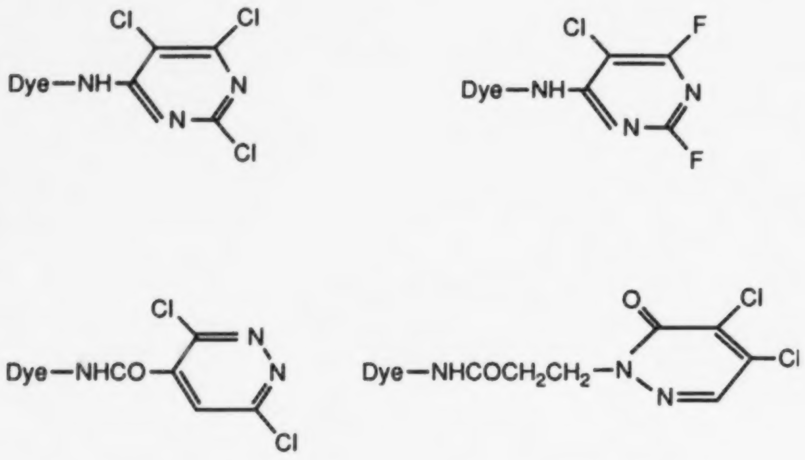
Reactive dyes are colored compounds capable of forming covalent bonds between the dye molecule and the fiber.[134] Cyanuric chloride plays an important role as a reactive dyes due to the reactivity of its chlorine atoms. The electronegative character of the ring nitrogen atoms and of the chlorine substituents induces a relative positive charge on the ring carbon atoms, which are thus highly susceptible to nucleophilic attack by molecules containing amino, hydroxyl, or alkoxyl groups. The first chlorine atom can be displaced by a nucleophile at 0 - 5 °C, the second at 35 - 40 °C, and the third at 80 - 85 °C (Equation 1-18).[135]

Equation 1-18:


Cl
N
N
Cl
N
Cl
PhNH2
0 - 5 °C
Base
NHPh
2 PhNH2
35 - 40 °C
Base
PhNH
NHPh
3 PhNH2
80 - 85 °C
Base

Other chloroheterocycles, particularly diazinyl types, have been shown to have similar functions as cyanuric chloride (Figure 1-21).[135]

Figure 1-21:

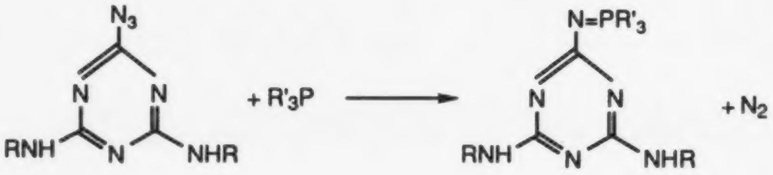


Cl
Cl
Dye—NH
N
N
Cl
Cl
F
Dye—NH
N
N
F
Cl
N
Dye—NHCO
N
Cl
O
Cl
Dye—NHCOCH₂CH₂—N
Cl
N

1.4.2. Phosphinimine Derivatives of Cyanuric Chloride

For use in a study of physiological activity,[136] a series of phosphinimine derivatives of cyanuric chloride has been reported.[136-139] The common synthetic method is the azide route (Equation 1-19).

Equation 1-19:

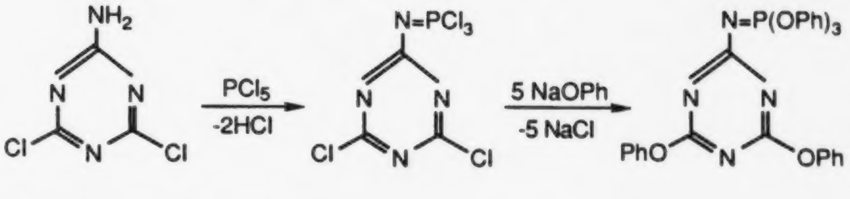


N₃
N
N
RNH
N
NHR
+ R'₃P
N=PR'₃
N
N
RNH
N
NHR
+ N₂

R = H, Alk; R' = Alk, Ar.

Another route was also reported which used the following reaction (Equation 1-20).[138]

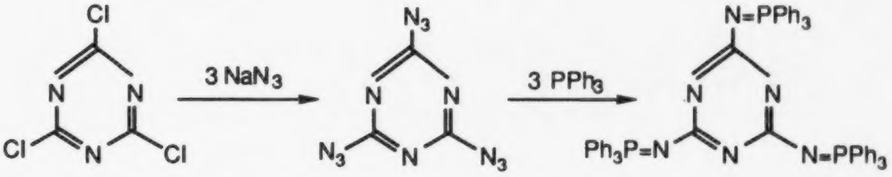
Equation 1-20:



NH2
N
N
Cl
N
Cl
PCl5
-2HCl
N=PCl3
N
N
Cl
N
Cl
5 NaOPh
-5 NaCl
N=P(OPh)3
N
N
PhO
N
OPh

Tris-phosphinimine derivatives of cyanuric chloride can be obtained *via* the azide route, since all three chlorines in cyanuric chloride can be substituted by azide groups (Equation 1-21).[137]

Equation 1-21:

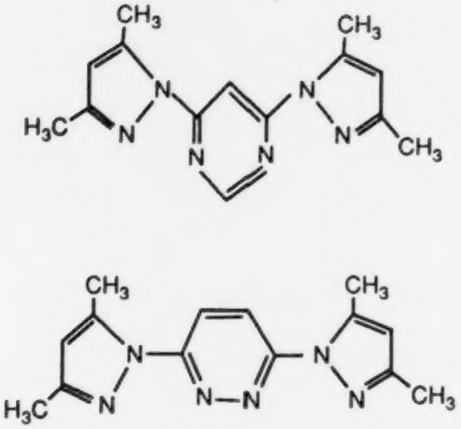


Cl
N
N
Cl
N
Cl
3 NaN3
N3
N
N
N3
N
N3
3 PPh3
N=PPh3
N
N
Ph3P=N
N
N=PPh3

1.4.3. Substituents of 3,5-Dimethylpyrazole Derivatives of Pyrimidine or Pyridazine and Their Cationic Rh(I) Complexes

There is no previous report of the introduction of pyrazole groups as substituents on cyanuric chloride. However, Uson et al.[140] reported introduction 3,5-dimethylpyrazole as substituents on pyrimidine and pyridazine. Both mono and disubstituted derivatives were reported (Figure 1-22).

Figure 1-22:


CH3
CH3
H3C
N
N
N
N
N
N
CH3
CH3
CH3
H3C
N
N
N—N
N
N
CH3

Their cationic Rh(I) complexes, $[Rh_n(diolefin)_n(L)](ClO_4)_n$, (diolefin = cod, tfb or nbd) were also reported.

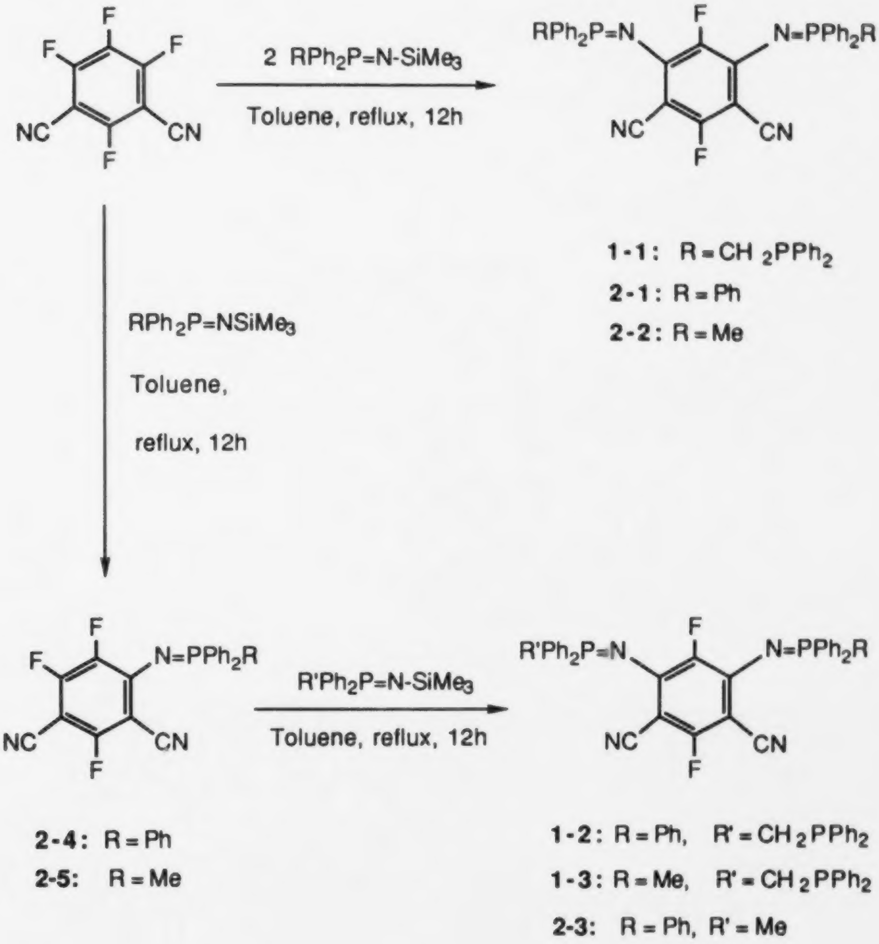
Chapter 2

Phosphinimine or Phosphinophosphinimine Substituted Fluoroaromatic Derivatives and Their Transition Metal Complexes

2.1. Synthesis, Characterization and Structures of New Multifunctional Fluoroaromatic Phosphinimine or Phosphinophosphoranimine Ligands

The reaction of 1,3-dicyanotetrafluorobenzene with two equivalents of trimethylsilyl phosphinimine in refluxing toluene gave the disubstituted fluoroaromatic derivatives (**1-1**) - (**1-3**) and (**2-1**) - (**2-3**) in good yield. In all cases fluorine atoms *para* to CN groups were substituted. Reactions proceeded smoothly with a 1:2 ratio of reagents to yield directly the corresponding disubstituted products. The reactions could be also carried out in a sequential, stepwise fashion, that is, using initially one equivalent of $R_3P=N-SiMe_3$ to form the monosubstituted derivatives (**2-4**) and (**2-5**), and then using a second equivalent of either the same or a different silyl phosphinimine to form the disubstituted derivatives. The silyl iminophosphorus reactant may be either a simple iminophosphorane, $R_3P=N-SiMe_3$, or the more complex bifunctional iminophosphoranophosphines such as $Ph_2PCH_2PPh_2=N-SiMe_3$ (Scheme 2-1).[4]

Scheme 2-1:


F
F
F
NC
CN
F
2 RPh$_2$P=N-SiMe$_3$
Toluene, reflux, 12h
RPh$_2$P=N
F
N=PPh$_2$R
NC
CN
F
RPh$_2$P=NSiMe$_3$
Toluene,
reflux, 12h
F
F
N=PPh$_2$R
NC
CN
F
R'Ph$_2$P=N-SiMe$_3$
Toluene, reflux, 12h
R'Ph$_2$P=N
F
N=PPh$_2$R
NC
CN
F

1-1: R = CH_2PPh_2
2-1: R = Ph
2-2: R = Me

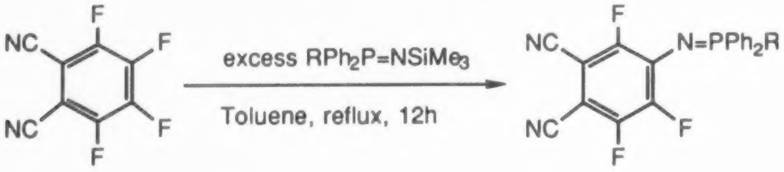
2-4: R = Ph
2-5: R = Me

1-2: R = Ph, R' = CH_2PPh_2
1-3: R = Me, R' = CH_2PPh_2
2-3: R = Ph, R' = Me

Five of these disubstituted ligands, (**1-1**), (**1-2**), (**2-1**), (**2-2**) and (**2-3**) have been structurally characterized. The mono and disubstituted fluoroaromatic compounds are each crystalline, air stable solids which are soluble in most common organic solvents. The disubstituted compounds are less soluble than the monosubstituted analogs. In the reactions shown in Scheme (2-1), the two fluorine atoms which are *para* to the electron withdrawing activating groups, CN, in 1,3-$(CN)_2C_6F_4$, are the most reactive and these fluorines are sequentially replaced. In contrast, only one of the fluorine atoms *para* to CN groups in 1,2-$(CN)_2C_6F_4$ could be eliminated to form the imine (Equation (2-1) (A)). The disubstituted derivatives could not be obtained.[5] This difference is in keeping with the expected electronic influence of the electron rich iminophosphorane. The introduction of the first substituent on the *para* site electronically deactivates both of the *ortho* positions required for second substitution (Equation 2-2, (A)) and the remaining *meta* fluorine is not labile.

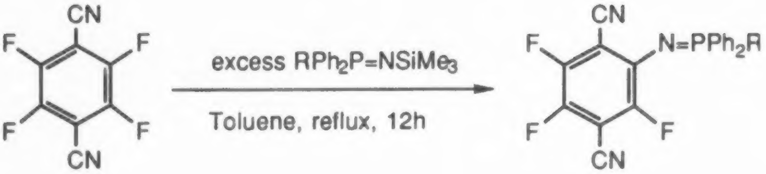
Equation 2-1:

(A)


NC
NC
F
F
F
F
excess RPh2P=NSiMe3
Toluene, reflux, 12h
NC
NC
F
N=PPh2R
F
F

2-6: R = Ph
2-7: R = Me

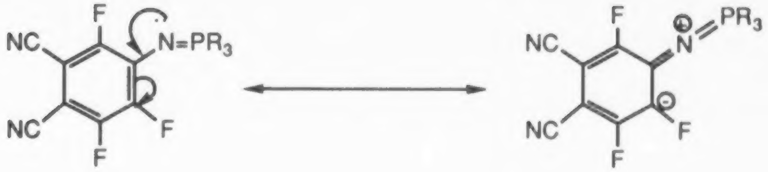
(B)


CN
F
F
F
F
CN
excess RPh2P=NSiMe3
Toluene, reflux, 12h
CN
F
N=PPh2R
F
F
CN

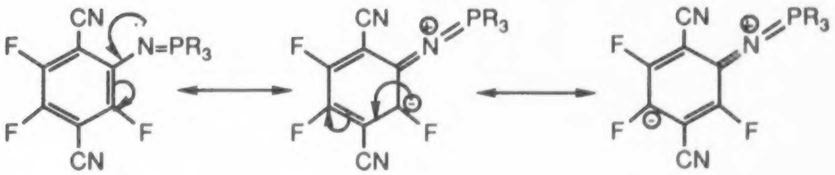
2-8: R = Ph
2-9: R = Me

Equation 2-2:

(A)



(B)

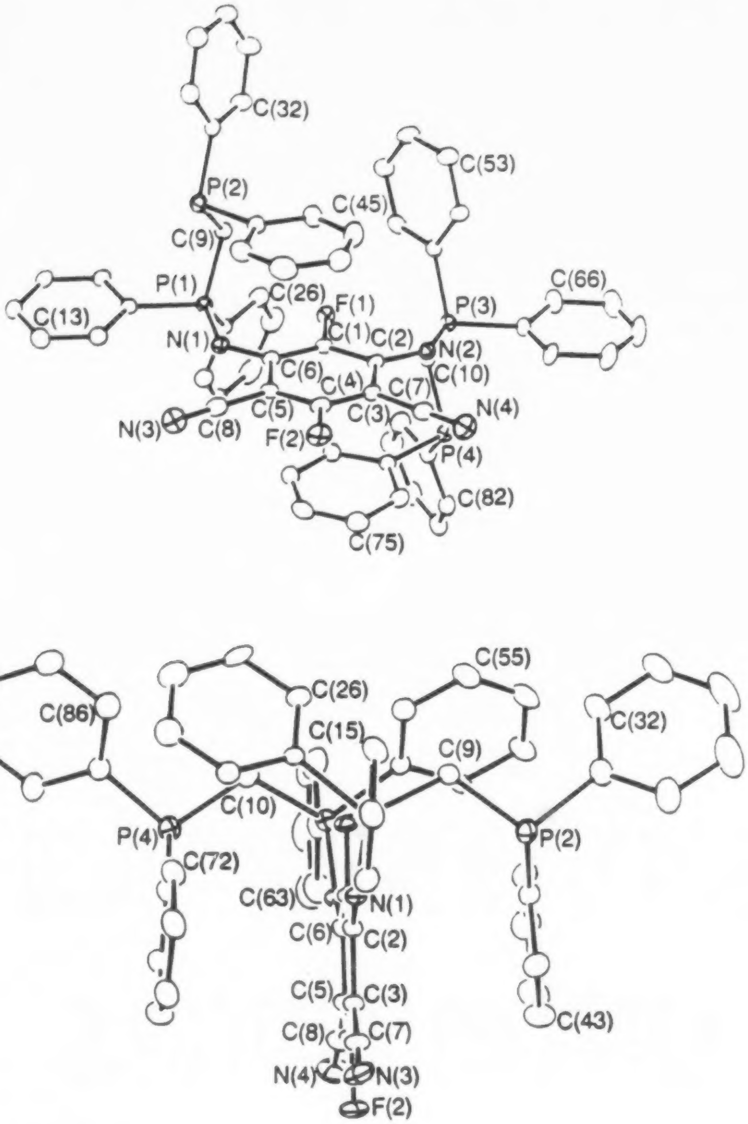


The isomer, 1,4-$(CN)_2C_6F_4$ which contains no F *para* to CN, can only be substituted *ortho* (or *meta*) to fluorine, and shows behavior similar to that of 1,2-$(CN)_2C_6F_4$. Only one fluorine in this 1,4 precursor can be eliminated to form the imine derivative (Equation 2-1, (B)). A second substitution was not achievable under the conditions used, for reasons similar to those advanced for 1,2-$(CN)_2C_6F_4$. Again, the first imine substituent electronically deactivates the remaining *ortho* and *para* positions, and further nucleophilic substitution does not occur at either of the remaining *ortho* or *para* positions (Equation 2-2, (B)).

The identification and molecular structure of each of the compounds has been determined from elemental analysis, mass spectra and ^1H, ^{31}P and ^{19}F NMR spectroscopy. Molecular ions for each of the compounds were observed in the mass spectra. Phosphorus-31 NMR data for ligands and complexes are given in Tables (2-1), (2-2) and (2-3), and the fluorine-19 NMR data are given in Table (2-4). The chemical shifts for both P^{III} and both P^{V} atoms in compound (**1-1**) indicate that the two PCPN groups are chemically equivalent. However when different phosphine imines are bound, the different environments are readily distinguished by their different chemical shifts. Compounds (**1-1**), (**1-2**) and (**1-3**) also show characteristic $^{2}J_{PP}$ values (49, 48 and 48 Hz respectively) which are about 4 - 5 Hz smaller than those obtained for analogous monosubstituted species (53 Hz).[5] The ^{31}P NMR spectra of disubstituted compounds (**2-1**) and (**2-2**) showed chemical shifts to high fields compared with the monosubstituted analogs, (**2-4**) and (**2-5**).

The crystal and molecular structures for (**1-1**), (**1-2**), (**2-1**), (**2-2**) and (**2-3**) have now been determined by X-ray diffraction[141], as representative examples of these new ligands. The ORTEP[142] plots for (**1-1**), (**1-2**), (**2-1**), (**2-2**) and (**2-3**) are shown in Figures (2-1) - (2-5) respectively.

The X-ray crystallographic data and the selected bonding parameters for these ligands are given in Tables (2-5) - (2-17). The structure of (**1-1**) shows considerable internal molecular regularity. The two remaining F atoms, the two CN groups and the two imine N atoms are almost co-planar with the carbons of the aromatic ring. One of the phenyl rings on each of the P^{V} centers is oriented approximately parallel to the fluoroaromatic ring (dihedral angles of 5.79° and 0.42°) and one of the phenyl rings on each of the P^{III} centers lies parallel to the fluoroaromatic ring. The two phenyl rings are arranged above and below the fluoroaromatic ring to form a sandwich of the fluoroaromatic ring, with an eclipsed orientation (dihedral angles of 4.73° and 5.98°). The dihedral angles are given in Table (2-18). In structure (**1-2**) similar features are observed; the dihedral angle is 3.7° Table (2-19). This eclipsed orientational structure is not uncommon in these molecular systems; similar relationships were previously observed in the structure of 4-(CN)$C_6F_4N=P(Ph)_2CH_2PPh_2$ (dihedral angle 19°) and 5-F-2,4-$(NO_2)_2C_6H_2N=P(Ph)_2CH_2PPh_2$ (dihedral angle 8°).[5] The X-ray crystallographic data for (**1-1**) - (**1-2**) and (**2-1**) - (**2-3**) show that the P-N bond in the phosphoranimines is a polar, higher order, short bond.[143,144] Thus the P-N bond lengths in (**1-1**), 1.569(4) and 1.581(3) Å, in (**1-2**), 1.585(4)Å (in the PCPN group) and 1.578(4)Å (in the $Ph_3P=N$ group), in (**2-1**), (1.579(2)Å, in (**2-2**), 1.570(4) and 1.589(3)Å, and in (**2-3**), 1.567(4) (for PPh_3 group) and 1.581(5)Å (for PPh_2Me group), are within the range of values for covalent radii (1.64Å)[145] for a double bond and are comparable to those obtained for $[N(PPh_3)_2]^+$ (1.60Å),[146] $Ph_2FP=NMe$ (1.641Å)[147] and $Ph_3P=NC_6H_4$-(*p*)-Br (1.56Å).[148] The P=N bond lengths observed in our compounds are, however, significantly longer than that in the prototypical precursor $Me_3SiN=P(Ph)_2CH_2PPh_2$ (1.529(3)Å),[149] following the general trend of longer P=N bonds and narrower P-N-X angles for those iminophophoranes which carry organic substitutents (even those which are highly electron withdrawing), in contrast to those which have silyl substitutents.[150]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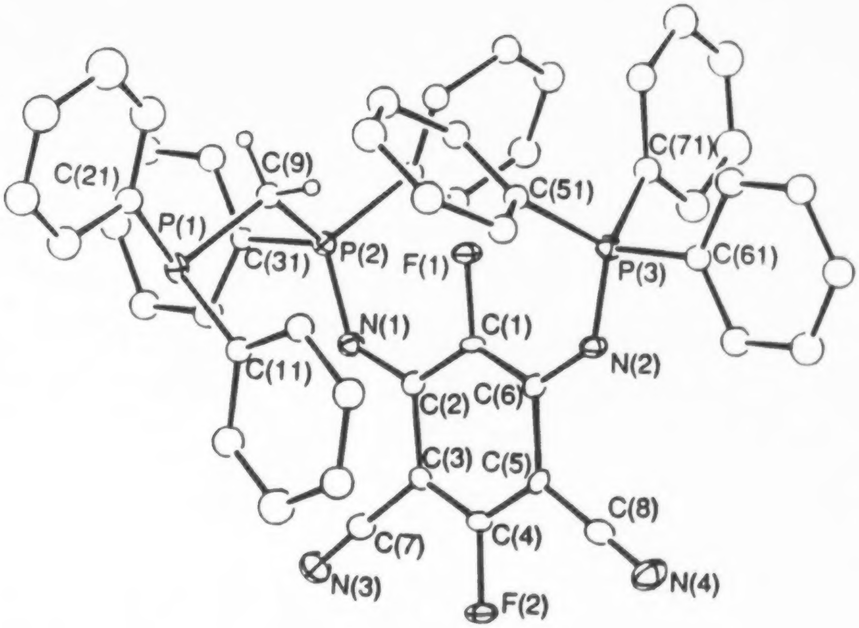
P(2)
C(45)
C(9)
C(66)
P(1)
C(26)
F(1)
P(3)
C(13)
C(1)
C(2)
N(1)
N(2)
C(6)
C(4)
C(10)
C(7)
C(5)
N(4)
C(3)
N(3)
C(8)
F(2)
P(4)
C(82)
C(75)
C(55)
C(26)
C(86)
C(15)
C(32)
C(9)
C(10)
P(4)
P(2)
C(72)
C(63)
N(1)
C(6)
C(2)
C(5)
C(3)
C(43)
C(8)
C(7)
N(4)
N(3)
F(2)

Figure 2-1. (Top): ORTEP perspective view of (**1-1**) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian eclipsoids at the 20% probability level. Hydrogen atoms are not shown. (Bottom): Alternate view of the molecule with the C1-C6 ring oriented almost edge-on.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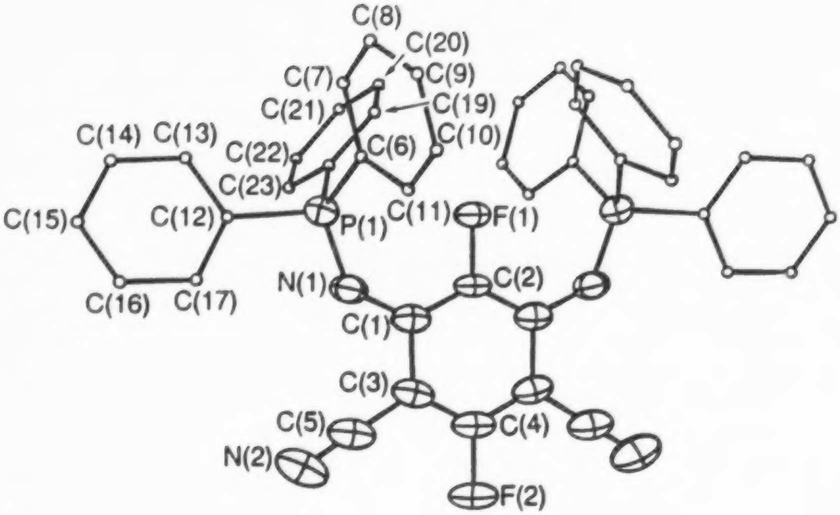
C(9)
P(1)
C(31)
P(2)
F(1)
C(51)
C(71)
P(3)
C(61)
N(1)
C(1)
N(2)
C(11)
C(2)
C(6)
C(3)
C(5)
C(8)
C(7)
C(4)
N(3)
F(2)
N(4)

Figure 2-2. ORTEP perspective view of (**1-2**) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian eclipsoids at the 20% probability level. The methylene hydrogens of the $N=PPh_2CH_2PPh_2$ group are shown artificially small, while those of the phosphine phenyl groups are not shown.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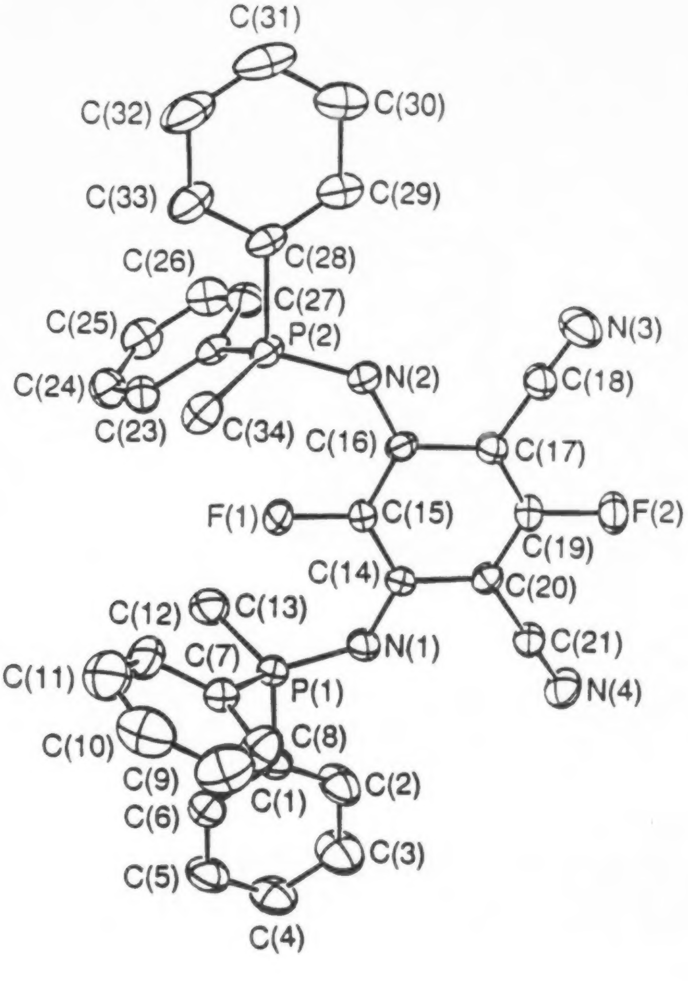
C(7)
C(9)
C(21)
C(19)
C(14)
C(13)
C(10)
C(22)
C(6)
C(23)
C(15)
C(12)
P(1)
C(11)
F(1)
N(1)
C(2)
C(16)
C(17)
C(1)
C(3)
C(5)
C(4)
N(2)
F(2)

Figure 2-3. ORTEP perspective view of (**2-1**) showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian elipsoids at the 20% probability level. Hydrogen atoms are not shown.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C(30)
C(33)
C(29)
C(28)
C(26)
C(27)
C(25)
P(2)
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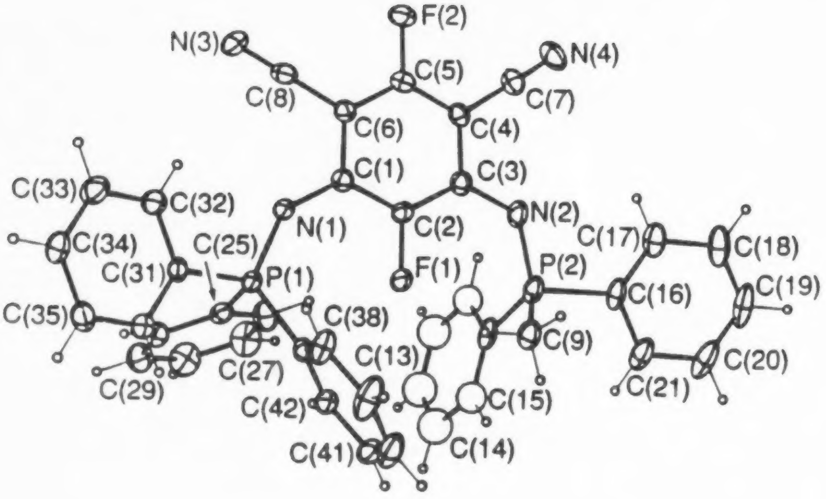
C(24)
N(2)
C(18)
C(23)
C(34)
C(16)
C(17)
F(1)
C(15)
F(2)
C(19)
C(14)
C(20)
C(12)
C(13)
N(1)
C(21)
C(11)
C(7)
P(1)
N(4)
C(10)
C(8)
C(9)
C(2)
C(1)
C(6)
C(3)
C(5)
C(4)

Figure 2-4. ORTEP perspective view of (**2-2**) showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian elipsoids at the 20% probability level. Hydrogen atoms are not shown.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N(3)
C(5)
N(4)
C(8)
C(7)
C(6)
C(4)
C(1)
C(3)
C(33)
C(32)
N(1)
C(2)
N(2)
C(17)
C(18)
C(34)
C(25)
C(31)
P(1)
F(1)
P(2)
C(16)
C(19)
C(35)
C(38)
C(9)
C(13)
C(27)
C(20)
C(29)
C(15)
C(21)
C(42)
C(41)
C(14)

Figure 2-5. ORTEP perspective view of (**2-3**) showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian elipsoids at the 20% probability level. Hydrogen atoms are shown.

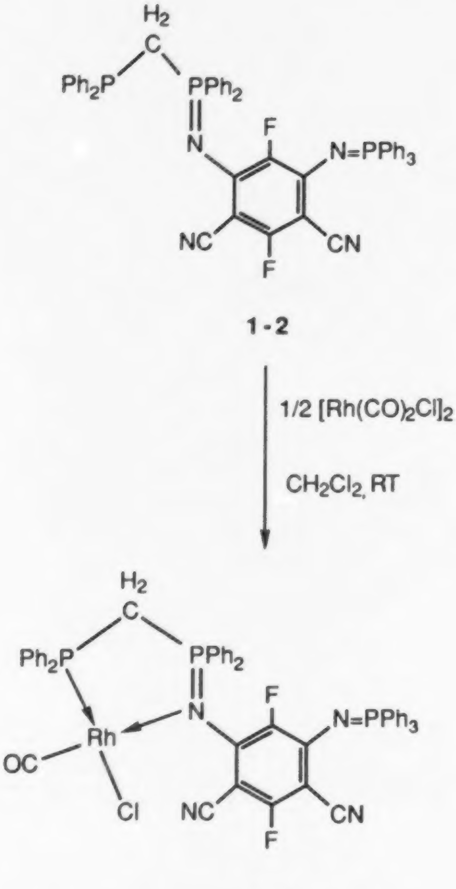
2.2. Complexation Reactions of the Ligands Containing Phosphinophosphoranimine with $[Rh(CO)_2Cl]_2$ and/or $Pd(cod)Cl_2$

2.2.1. Complexation Reactions of Ligands (1-1) and (1-2) with $[Rh(CO)_2Cl]_2$

Compound (**1-2**) reacts with one-half equivalent of $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 at 25 °C to give complex (**1-4**) in high yield (Equation 2-3).

The ^{31}P NMR chemical shifts of the P^{III} and P^{V} centers in complex (**1-4**) are very similar to those found for the known complexes $\mathrm{\overline{RN{=}P(Ph)_2CH_2P(Ph)_2Rh}(CO)Cl}$,[5,6] in which the imine nitrogen carries fluoroaromatic or dinitro aromatic substituents (R). However, in (**1-4**) the signal arising from the uncomplexed $Ph_3P{=}N$ unit is shifted to low field by about 3.5 ppm, suggesting some additional electron delocalization from the fluoroaromatic ring occurs in this complex. Direct P^{III}-Rh bonding is clearly indicated by the large, characteristic $^{1}J_{PRh}$ value. The ν_{CO} value of 1970 cm^{-1} (Table (2-4)) indicates that the CO group coordinated to Rh is located *cis* to the P^{III} center.[5]

Equation 2-3:


H2
C
Ph2P
PPh2
N
F
N=PPh3
NC
CN
F
1/2 [Rh(CO)2Cl]2
CH2Cl2, RT
Rh
OC
Cl

1-2

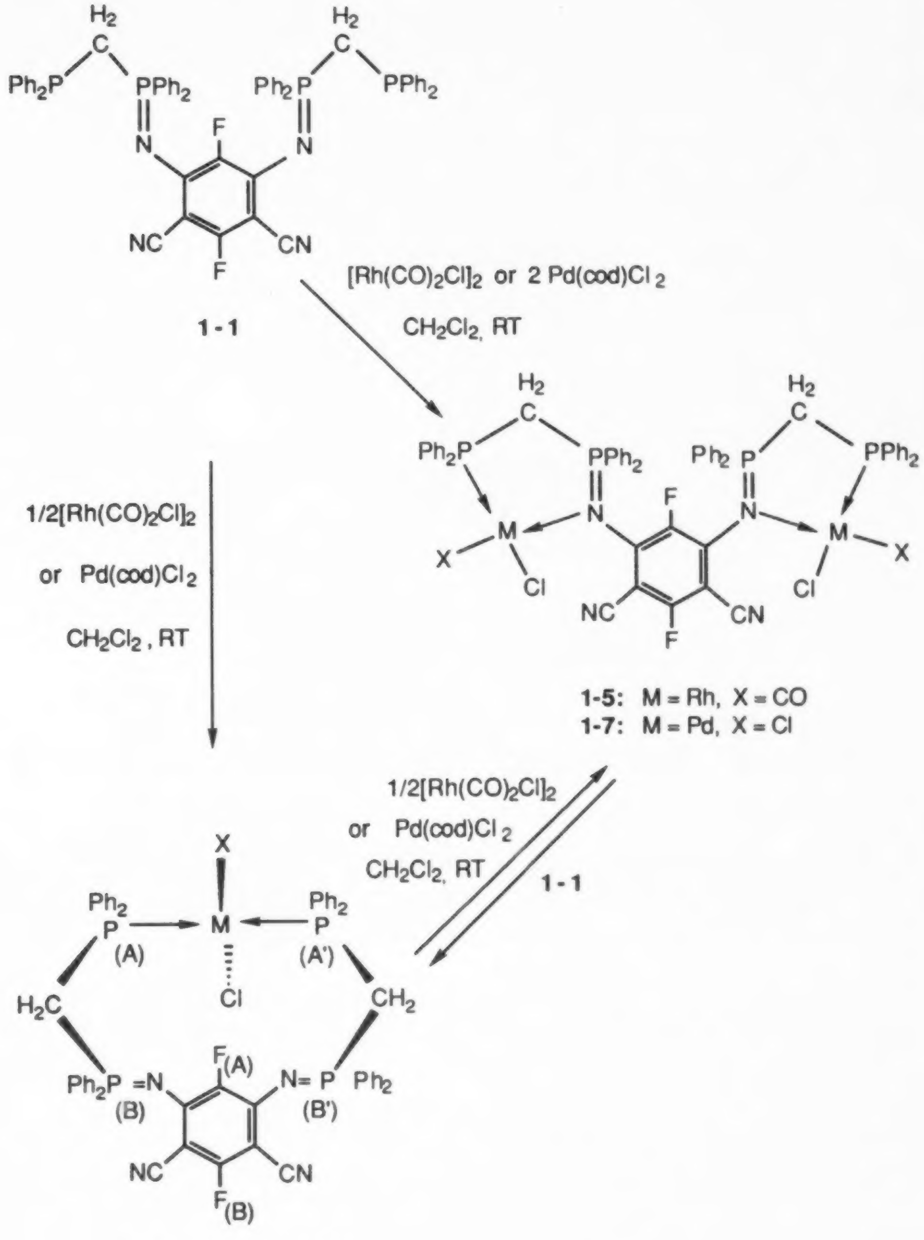
1-4

Compound (**1-1**) reacts with one molar equivalent of $[Rh(CO)_2Cl]_2$ to give the dinuclear complex (**1-5**) in which both coordination sites are occupied (Scheme 2-2).

Reacting (**1-1**) with one-half equivalent of $[Rh(CO)_2Cl]_2$ gives the *trans* complex (**1-6**), in which only one Rh atom is complexed by the ligand (Scheme 2-2). Reaction of (**1-6**) with another equivalent of Rh precursor at room temperature in CH_2Cl_2 gives the dinuclear product (**1-5**). The process can be reversed by treating

(**1-5**) with one equivalent ligand (**1-1**), again at room temperature in CH_2Cl_2, to produce the mononuclear *trans* complex (**1-6**).

Scheme 2-2:


[Rh(CO)2Cl]2 or 2 Pd(cod)Cl 2
CH2Cl2, RT
1/2[Rh(CO)2Cl]2
or Pd(cod)Cl2
CH2Cl2, RT
1/2[Rh(CO)2Cl]2
or Pd(cod)Cl 2
CH2Cl2, RT
1-1
(A)
(A')
(B)
(B')
F(A)
F(B)

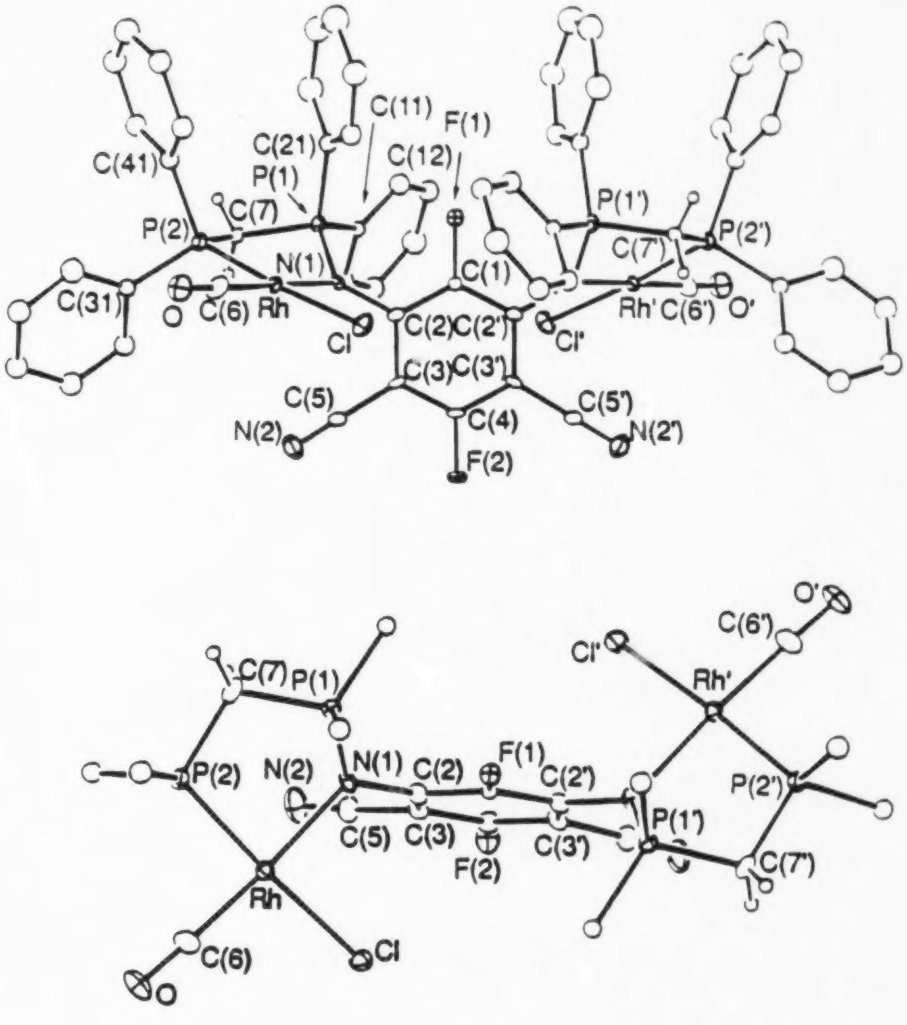
1-1

1-5: M = Rh, X = CO
1-7: M = Pd, X = Cl

1-6: M = Rh, X = CO
1-8: M = Pd, X = Cl

The NMR data of (**1-5**) show that the two Rh centers are equivalent, with ^{31}P chemical shifts of the P^{V} and P^{III} centers being similar to those of the monosubstituted analogs. The P^{III} signal is strongly shifted (by 68 ppm) to low field upon coordination, and the P^{V} signal, a broad, poorly resolved doublet, is similarly shifted (by 32 ppm) relative to the free ligand. The fluorine located between the two CN groups in (**1-5**) shows no substantial change in the NMR chemical shift upon complexation of the ligand to the metal, but the fluorine located between the imine nitrogens is shifted by 22 ppm to low field upon complex formation. The structure (*vide infra*) shows that this fluorine is located very close to two of the phenyl groups, one on each of the two P^{V}centers, and the observed lowfield shift probably reflects the deshielding by this phenyl group environment. Similar behaviour was also observed for complex (**1-4**). In that case, the ^{19}F chemical shift of the fluorine atom which is located ortho to the P^{V} was shifted by 16 ppm to low field, suggesting that one of the phenyl substituents on P^{V} lies physically close to this fluorine. The CO ligand stretching frequency of (**1-5**) is 1979 cm^{-1}, consistent with a *cis* phosphine-carbonyl structure.[5] The ^{1}H NMR spectrum in the CH_2 region showed two signals implying two inequivalent environments for the hydrogens of each methylene group.

The molecular structure of (**1-5**) was determined[141] by X-ray diffraction. The ORTEP[142] plot is shown in Figure 2-6.


C(11)
F(1)
C(21)
C(12)
C(41)
P(1)
C(7)
P(2)
N(1)
C(1)
P(1')
C(7')
P(2')
C(31)
O
C(6)
Rh
Cl
C(2)
C(2')
Cl'
Rh'
C(6')
O'
C(3)
C(3')
C(5)
C(5')
N(2)
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F(2)
O'
C(6')
Cl'
Rh'
C(7)
P(1)
N(1)
C(2)
F(1)
C(2')
P(2)
N(2)
P(2')
C(5)
C(3)
C(3')
P(1')
F(2)
C(7')
Rh
C(6)
Cl
O

Figure 2-6. (Top): ORTEP perspective view of (1-5) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian eclipsoids at the 20% probability level. The dppm methylene hydrogens are shown artificially small, while those of the phosphine phenyl groups are not shown. (Bottom): Top view of the molecule.

The structural parameters for (**1-5**) and the bonding parameters are given in Tables (2-5), (2-9), and (2-20) - (2-22). The structure comprises the neutral dinuclear complex $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}[\overline{N{=}P(Ph)_2CH_2P(Ph)_2R}h(CO)Cl]_2$, (**1-5**), and an uncoordinated co-crystallized molecule of CH_3CN. The complex shows a square planar geometry about each Rh(I) with the CO *cis* to the phosphine, as indicated by the IR spectrum. Bond angles and lengths are typical for a square planar chelate of Rh(I). The P(1)-N(1) distance of 1.61(1) Å in the complex is within the range found for a coordinated iminophosphoranyl group.[5] The directly bound Rh-P^{III} distance of 2.206(4) Å also lies within the range found in many Rh(I) phosphine complexes of the type $P_2Rh(CO)Cl$.[151-157] The molecule has C_2 symmetry with the two fluorine atoms and the carbons to which they are attached being located on a crystallographic twofold axis. These two F atoms, two CN groups and two imine N atoms are coplanar with the fluoroaromatic ring. The Cl, Rh, C(6), O, N(1), P(2) and C(7) atoms are almost coplanar, (Table (2-22)) while P(1) lies significantly above the plane, by 0.722Å. The dihedral angle between the Rh-P(2)-C(7)-N(1) and C(7)-P(1)-N(1) planes is 133.3°. The view shown in the lower structure of Figure 2-6 clearly shows that one Rh lies below and the other lies above the fluoroaromatic ring. The dihedral angle between the Rh-P(2)-C(7)-N(1) plane and the fluoroaromatic ring is 76.0°. Complete dihedral angle data are given in Table (2-22).

Compared with our previously described Rh complexes,[5,158,159] and the above described dinuclear complex, the mononuclear complex (**1-6**) is unusual. First, ^{31}P NMR data indicate that the two PCPN groups are symmetrically coordinated to Rh. We therefore surmise that the two P^{III} units must be coordinated to the Rh metal center and that they must be in a mutual *trans* relationship. The presence of a large coupling of P^{III} to rhodium ($^1J_{PRh}$) allows ready identification of the ^{31}P signal for P^{III} and shows that this signal lies to lower field than that for P^V. Thus the P^{III} has shifted by about 54 ppm to low field upon coordination (as in (**1-5**) and (**1-4**)) whereas the P^V signal has shifted instead to high field by about 10 ppm. The $^1J_{PRh}$ value of 128.6 Hz, (obtained by analysis of the second order spectrum) is also smaller than expected. For the ^{19}F NMR spectrum, the fluorine which lies between the two P^V imines is not as greatly affected as was the case in (**1-5**), and has only been shifted by 4 ppm to low field upon complexation. This suggests that in this case the phenyl rings subtended on P^V are not proximate to this fluorine, in contrast to (**1-4**). The spectral pattern is a doublet of triplets of triplets, which indicates coupling to the other fluorine, two P^V and two P^{III} respectively. The signal for the other fluorine is a doublet of triplets, clearly arising from the coupling to one other fluorine and to two P^V, but not to the remote P^{III} centers. The ^{31}P NMR spectrum was clearly second order, and showed complex multiplets for both P^{III} and P^V signals. The spectral pattern for (**1-6**) is shown in Figure 2-7 (top). A large coupling between Rh and P^{III} is readily observed which clearly identifies this low field signal as that arising from the P^{III} center. The P^V signal is therefore the higher field signal, which is in contrast to related compounds in the system but which is consistent with the proposed formulation. In this case the imine N of the PCPN unit is not coordinated to the Rh center and so the P^V signal is not substantially shifted by coordination. The coupling patterns cannot be clearly resolved, in contast to the usually clearly defined features in spectra of compounds of this type. Homonuclear $^{31}P\{^{31}P\}$ NMR decoupling measurements (Figure 2-7, bottom) applied to the P^V signal reduced the P^{III} pattern to a doublet of doublets, the smaller doublet probably arising from the coupling of F1 with P^{III}. When applied to the P^{III} signal, homonuclear decoupling reduces the P^V pattern to a doublet of doublets, which indicates that P^V couples to two different fluorines (Fig. 2-7, bottom), as expected from the ^{19}F NMR spectra. These experiments themselves did not reveal sufficient information to fully determine the coupling interactions between P^{III} and P^V.

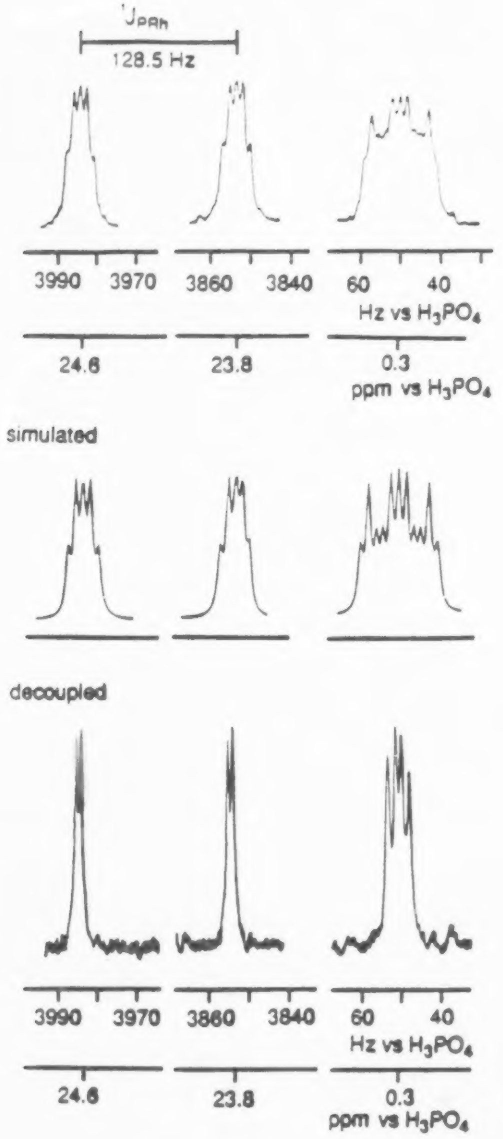


Figure 2-7. ^{31}P NMR spectra of (**1-6**), (Top): experimental spectrum; (Center): simulated spectrum and (Bottom): with homonuclear $^{31}P\{^{31}P\}$ decoupling applied to P^V and P^{III} respectively.

The pattern of the spectrum was however successfully simulated (Figure 2-7, center) with the fit shown. The simulation data are listed in Table (2-23). The successful spectral simulation suggests that the two P^{III} centers and the two P^{V} centers are each chemically equivalent, but that magnetic inequivalence leads to the observed second order behavior. The coupling constants used for the simulation, $^{2}J_{P(A)\text{-}P(B)} = {}^{2}J_{P(A')\text{-}P(B')} = 1.85$ Hz and $^{4}J_{P(A)\text{-}P(B')} = {}^{4}J_{P(A')\text{-}P(B)} = 1.75$ Hz, show only a very small difference (0.10 Hz) relative to each other, but the values are reliable because small changes in either of the coupling constant values used makes a large difference in the calculated spectral pattern and destroys the match with the experimental spectrum.

The ^{1}H NMR spectrum of the CH_2 region of (**1-6**), similar to that for (**1-5**), showed two different signals, each one showing a doublet of doublet of doublets pattern. The two hydrogens on each methylene carbon therefore have different magnetic environments; each hydrogen is coupled to the other hydrogen on the CH_2 bridge and to two different phosphorus centers.

The NMR spectral behavior is therefore consistent with the formulation of complex (**1-6**) as a bis-phosphine complex of Rh(I) in which the long "arms" of the ligand (**1-1**) are able to span the *trans* positions of the square plane to form a 12 membered macrocyclic ring. This is favoured by the affinity of Rh(I) for a P^{III} donor. It would be interesting to see if internal coupling reactions could be done within this structure as the resultant bicyclic ring structure should not suffer extraordinary strain. However, such experiments have not yet been attempted.

The stretching frequencies of the CN groups in the ligands are slightly reduced compared with those displayed by the starting material, 1,3-$(CN)_2C_6F_4$. These data are compared with that from other related compounds, such as 2,4-$(CN)_2C_6F_3N{=}PPh_3$,(*vide infra*) 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_3)_2$(*vide infra*) and

$2,4\text{-}(CN)_2C_6F_3N{=}P(Ph)_2CH_2PPh_2$ (Table (2-15)).[6] The order of Δ, the difference in ν_{CN} relative to the parent cyanobenzene, indicates that reducing the electronegativity of the substituent (or increasing the donor capability of the substituent) leads to more electron delocalization involving the CN groups, and therefore to a greater decrease of the CN stretching frequencies. Thus, $N{=}P(Ph)_2CH_2PPh_2$ is a better electron donor than $N{=}PPh_3$.

The influences of R_1 and R_2 on ν_{CN} are additive. When $R_1 = F$, $R_2 = (N{=}PPh_3)$, a decrease of 15 cm^{-1} for ν_{CN} is observed whereas when $R_1 = R_2 = (N{=}PPh_3)$, the decrease is 35 cm^{-1} which is slightly more than twice the value of the former. When $R_1 = F$, $R_2 = (N{=}P(Ph)_2CH_2PPh_2)$, a decrease of 21 cm^{-1} is observed whereas when $R_1 = R_2 = (N{=}P(Ph)_2CH_2PPh_2)$, the decrease is 47 cm^{-1} which again is slightly more than twice the value of the former. In the case of $R_1 = (N{=}PPh_3)$, $R_2 = (N{=}P(Ph)_2CH_2PPh_2)$, a decrease of 38 cm^{-1} is observed and this value is only slightly greater than the sum of the individual contribution of the two groups. Dividing these shift decrements into components due to each group gives a decrement of 16 - 18 cm^{-1} for a $N{=}PPh_3$ group and approximately 24 cm^{-1} for the diphosphorus substituent, relative to the original fluorine substituent.

Many complexes are known which contain uncoordinated CN groups and for these there is no systematic shift of the CN stretching frequency upon coordination of the remote site. The value of the IR band for the complex may be either higher or lower than that shown by the uncoordinated ligand.[7] Herein we observe that the stretching frequencies of the uncoordinated CN groups in our metal complexes are in all cases higher than those for the corresponding IR bands in the uncomplexed ligands (Table 2-2). Some shifts are very small; e.g. in complex (**1-4**), $\nu_{CN} = 2217$ cm^{-1}, whereas in ligand (**1-2**) $\nu_{CN} = 2214$ cm^{-1}, an increase of only 3 cm^{-1} upon coordination. The small shift indicates that the environment of the CN substituent is not greatly perturbed by coordination in this case. In contrast, for complex (**1-5**), $\nu_{CN} = 2227$ cm^{-1}, an increase of 22 cm^{-1} is found upon complexation compared to the value for uncoordinated ligand (**1-1**) ($\nu_{CN} = 2205$ cm^{-1}). Similarly the band for the mononuclear complex (**1-6**) ($\nu_{CN} = 2216$ cm^{-1}) shows an increase relative to the band for the ligand of 11 cm^{-1}, which is half as large as the coordination shift in the binuclear complex (**1-5**). The difference between CN bond lengths in ligand (**1-1**) (1.140(6) Å) and in the metal complex (**1-5**) (1.12(1)Å) is not sufficiently great to indicate any trends or correlations between stretching frequency and bond length or strength.

2.2.2. Complexation Reactions of (1-1) with Pd(cod)Cl$_2$

In a series of reactions similar to those for the Rh analogs, compound (**1-1**) reacts with two equivalents of Pd(cod)Cl$_2$ and one equivalent of Pd(cod)Cl$_2$ at room temperature in CH_2Cl_2 to give the dinuclear product (**1-7**) and the mononuclear product (**1-8**) respectively (Scheme 2-2).

Ions corresponding to a parent peak minus one chlorine are observed in the mass spectra for both compounds (**1-7**) and (**1-8**). The IR data show CN stretching frequencies at 2228 cm^{-1} and 2215 cm^{-1} for (**1-7**) and (**1-8**) respectively, which are almost the same values as in compounds (**1-5**) and (**1-6**). The NMR data of (**1-7**) and (**1-8**) show that their structures are similar to the Rh analogs (**1-5**) and (**1-6**). For (**1-7**), the ^{31}P NMR spectra show two doublets at 50.7 ppm and 19.7 ppm respectively. Coupling between phosphorus and fluorine is not observerd. For (**1-8**), the ^{31}P NMR spectra show two peaks at 5.8 ppm and 0.0 ppm respectively, and the shape of the peaks is very similar to those of (**1-6**), except that they are not as well resolved.

Again, like the Rh analogs, the mononuclear product (**1-8**) can be converted to the dinuclear complex (**1-7**) on reaction with a further equivalent of the Pd precursor, and the dinuclear complex (**1-7**) can also be converted to (**1-8**) by reacting with one equivalent of ligand (**1-1**).

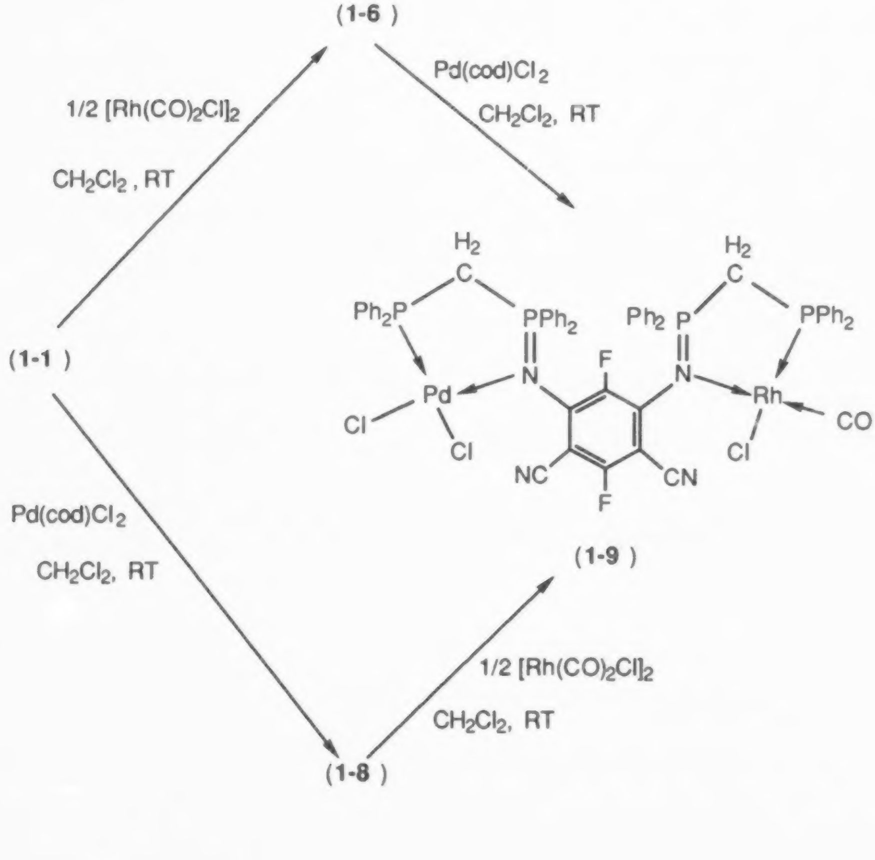
2.2.3. Mixed Dimetallic Complex of Rh and Pd of Ligand (1-1)

$4,6\text{-}(CN)_2\text{-}C_6F_2\text{-}1\text{-}[\overline{N{=}P(Ph)_2CH_2P(Ph)_2Rh}(CO)Cl]\text{-}3\text{-}[\overline{N{=}P(Ph)_2CH_2P(Ph)_2Pd}Cl_2]$

(**1-9**)

Compound (**1-9**) can be obtained, either by reacting (**1-6**) with one equivalent of Pd(cod)Cl_2, or by reacting (**1-8**) with one half equivalent of $[Rh(CO)_2Cl]_2$ (Scheme 2-3).

Scheme 2-3:


(1-6)
1/2 [Rh(CO)2Cl]2
CH2Cl2 , RT
Pd(cod)Cl2
CH2Cl2, RT
(1-1)
Pd(cod)Cl2
CH2Cl2, RT
H2
C
Ph2P
PPh2
Pd
Cl
Cl
N
F
NC
F
CN
N
Ph2 P
H2
C
PPh2
Rh
CO
Cl
(1-9)
1/2 [Rh(CO)2Cl]2
CH2Cl2, RT
(1-8)

The ^{31}P NMR data showed that the product contained mainly product (**1-9**), and lesser amounts of the Rh-Rh complex (**1-5**) and Pd-Pd complex (**1-7**). The ratio obtained was 9:1:1 for Rh-Pd : Rh-Rh : Pd-Pd using either pathway. In the ^{31}P NMR spectrum (Figure 2-8), two doublets at 48.9 ppm and 16.5 ppm are assigned to the Pd side of the complex, which are shifted upfield by 1.8 ppm and 3.2 ppm respectively compared with that of Pd-Pd complex(**1-7**); the doublet at 42.4 ppm (P^V) and the doublets at 39.6 and 37.6 ppm (P^{III}) are assigned to the Rh side of the complex. The signal for P^V only shifted downfield about 0.8 ppm compared with that of Rh-Rh complex (**1-5**), and the signals for P^{III} ($^1J_{PIII-Rh}$ = 164 Hz) are almost overlapped by those for the Rh-Rh complex. In the mass spectrum the peaks corresponding to the parent peak minus one chlorine are observed. The IR spectrum showed $\nu_{CO} = 1979$ cm^{-1} and $\nu_{CN} = 2228$ cm^{-1}, which are essentially the same values as for the Rh-Rh complex (**1-5**).

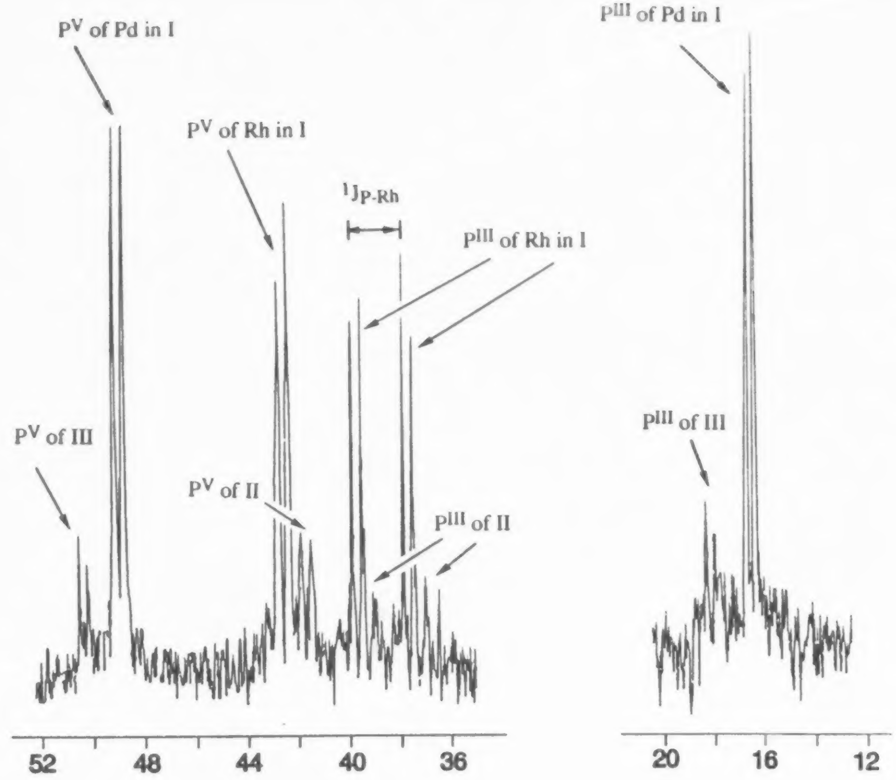


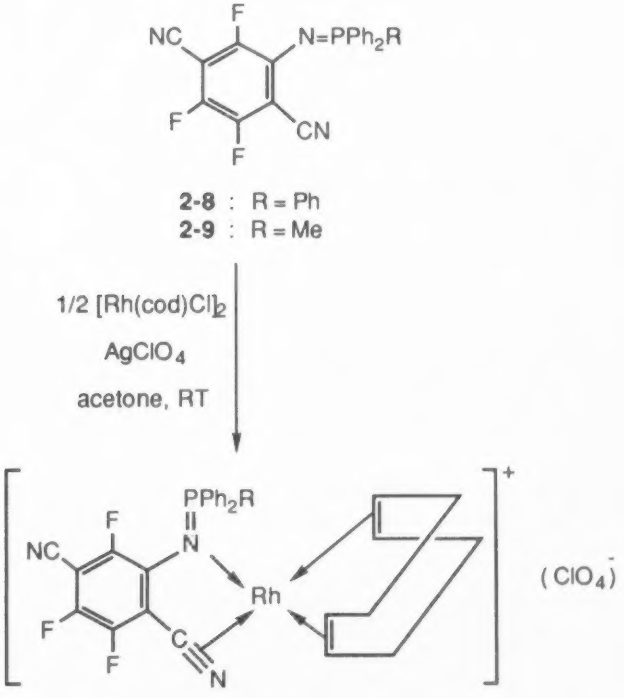
Figure 2-8. ^{31}P NMR spectrum for the mixed dimetallic complex (**1-9**). I: Rh-Pd complex (**1-9**); II: Rh-Rh complex (**1-5**); III: Pd-Pd complex (**1-7**).

2.3. Cationic Rh(I) Complexes of Cyano σ or π Coordinated Mono and Disubstituted Cyanofluoroaromatic Phosphinimine Ligands

2.3.1. Formation of Cationic (cod)Rh(I) Complexes: Examples of π Bonded CN Substituents

Reactions of (**2-8**) and (**2-9**) with 1/2$[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C gave the complex, (**2-10**), $[5\text{-}(CN)\text{-}C_6F_3\text{-}2\text{-}(\pi\text{-}CN)\text{-}1\text{-}(N{=}PPh_3)Rh(cod)](ClO_4)$ and (**2-11**), $[5\text{-}(CN)\text{-}C_6F_3\text{-}2\text{-}(\pi\text{-}CN)\text{-}1\text{-}(N{=}PPh_2Me)Rh(cod)](ClO_4)$ respectively (Equation 2-4).

Equation 2-4:


F
NC
N=PPh2R
F
CN
F
2-8 : R = Ph
2-9 : R = Me
1/2 [Rh(cod)Cl]2
AgClO4
acetone, RT
PPh2R
F
NC
N
Rh
F
F
C
N
+
(ClO4-)

2-10 : R = Ph
2-11 : R = Me

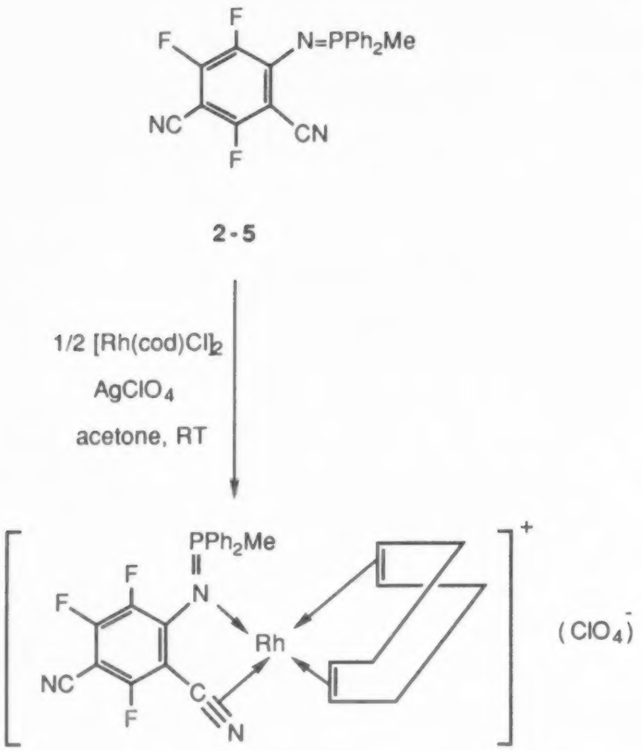
Formulae corresponding to the cationic monometallic complexes were observed in the mass spectra (FAB) for both (**2-10**) and (**2-11**). The ^{31}P NMR showed a 3.1 ppm and 5.7 ppm downfield shift of the phosphorus signals compared with the corresponding ligands respectively. No pronounced differences were observed between the ligands and the complexes in the ^{19}F NMR spectra. The CN stretching frequencies for complex (**2-10**) appeared at 2253 and 2009 cm^{-1}, whereas the uncoordinated ligand (**2-8**) showed two peaks at 2240 and 2230 cm^{-1}. The corresponding ligands for complex (**2-11**) appeared at 2245 and 2011 cm^{-1} compared with those for ligand (**2-9**) at 2225 and 2213 cm^{-1}. Thus, in each case the higher frequency peak of the free ligand shifts to higher frequency on coordination, 15 cm^{-1} for (**2-10**) and 20 cm^{-1} for (**2-11**). The lower frequency ligand CN band, shifts to a significantly lower frequency on coordination. The coordination shift for (**2-10**) is 221 cm^{-1} and for (**2-11**) is 202 cm^{-1}. Reversing this correlation changes the numerical shift values, but does not alter the general conclusion. Thus, for each complex one CN band is shifted by a relatively small amount compared to those for the free ligand, consistent with the association of the higher frequency band with the CN group which relatively unaffected by coordination. The CN vibration which is at a substantially lower value than for the free ligand is assigned to the π-coordinated nitrile. The nitrile is coordinated in a "side on" manner, and so the corresponding IR band would be expected to be reduced substantially by interaction with the metal center. We have elsewhere observed in similar complexes, only small CN frequency increases in the uncoordinated nitrile substituents upon coordination of other parts of the ligand to the metal (see earlier of this Chapter) and the present data are consistent with this trend.

The most common σ-coordination mode for nitrile ligands uses the nitrile lone pair of the nitrogen, and in these cases the CN stretching frequency may shift to either higher or lower frequency.[7] In this mode, donation from the RCN ligand of the lone pair on nitrogen, which is likely an orbital of some antibonding character (*vide infra*), to the metal in a R-CN→ML_n complex, leads to a situation in which the antibonding character decreases upon coordination of the ligand to transition metals. As a result, the CN bond order is increased, and consequently the CN stretching frequency increases. However, if π back donation from a transition metal to the CN π* orbitals occurs, it results in a decrease in the CN bond order and a corresponding decrease in the stretching frequency. Alternatively, if the transition metal is in a high oxidation state, there is little or no π back donation. In such cases the CN bond is strengthened and the net observed effect is an increase in the CN stretching frequency.

The alternative coordination mode for CN is to bind as a side-on bonded ligand using the CN triple bond. Although rare, a few instances of such π coordinated nitrile interaction have been reported (see Chapter 1). In this case, the CN stretching frequencies will shift to lower frequencies and the shifts will be large because the CN bond will be reduced in order. Complex (**2-10**) shows a decrease of 221 cm^{-1}, which is a typical shift for previously known "side-on" bonded CN ligands. Thus the large negative shift in ν_{CN} supports the interpretation of a side-on π bonded CN interaction in complex (**2-10**).

A similar reaction of (**2-5**) with 1/2$[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C gave the complex (**2-12**), [4-(CN)-C_6F_3-2-(π-CN)-1-(N=PPh_2Me)Rh(cod)](ClO_4) (Equation 2-5).

Equation 2-5:


F
F
N=PPh$_2$Me
NC
CN
F
2-5
1/2 [Rh(cod)Cl]$_2$
AgClO$_4$
acetone, RT
PPh$_2$Me
F
F
N
Rh
NC
F
C
N
+
(ClO$_4^-$)

2-12

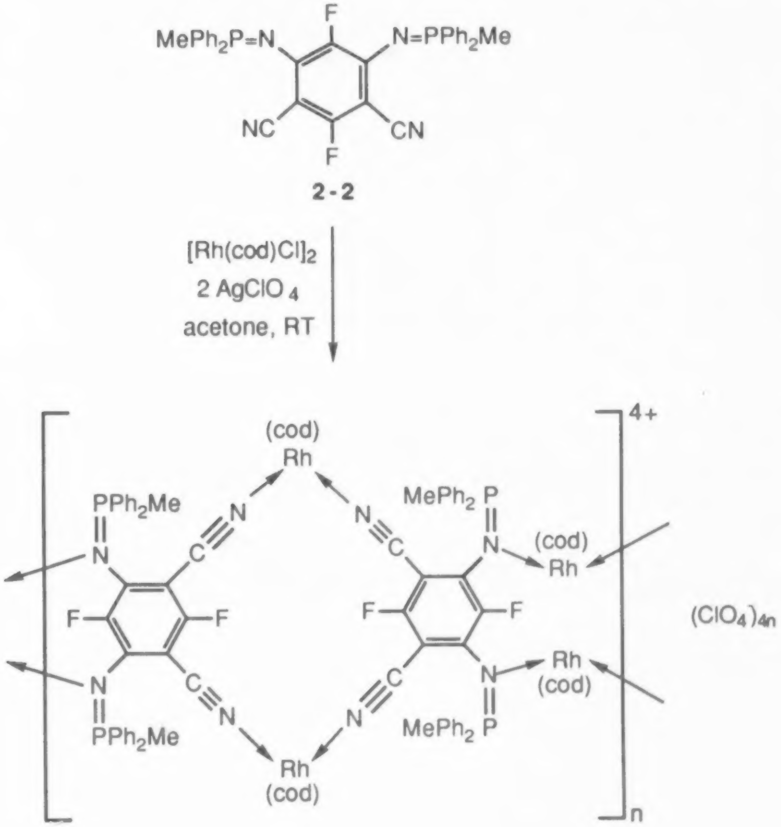
The proposed formulation of complex (**2-12**) is supported by the observation of the molecular monometallic cation of the complex in the mass spectra (FAB). The ^{31}P NMR spectrum showed a 5.4 ppm downfield shift for the phosphorus signal compared with the uncoordinated ligand. There was no significant change between the ^{19}F NMR spectra of the complex and ligand. The IR spectrum of the complex showed CN stretching bands at 2253 cm^{-1} and 2014 cm^{-1}, whereas the ligand showed only one peak at 2233 cm^{-1} (which is probably the expected pair of peaks overlapped). Again, we can assign the higher frequency in the complex to a band shifted to high frequency

($\Delta = 20$ cm^{-1}) corresponding to the free, uncoordinated CN group. The lower frequency band can be assigned to a CN band greatly shifted to lower frequency ($\Delta = 219$ cm^{-1}) by side-on coordination to the metal.

2.3.2. Formation of Cationic (cod)Rh(I) Complexes: σ Bonded CN Substituents

The reaction of the doubly imine-substituted ligand (**2-2**) with $[Rh(cod)Cl]_2$ and two equivalents of $AgClO_4$ in acetone at 25 °C gave the complex, (**2-13**) (Equation 2-6).

Equation 2-6:

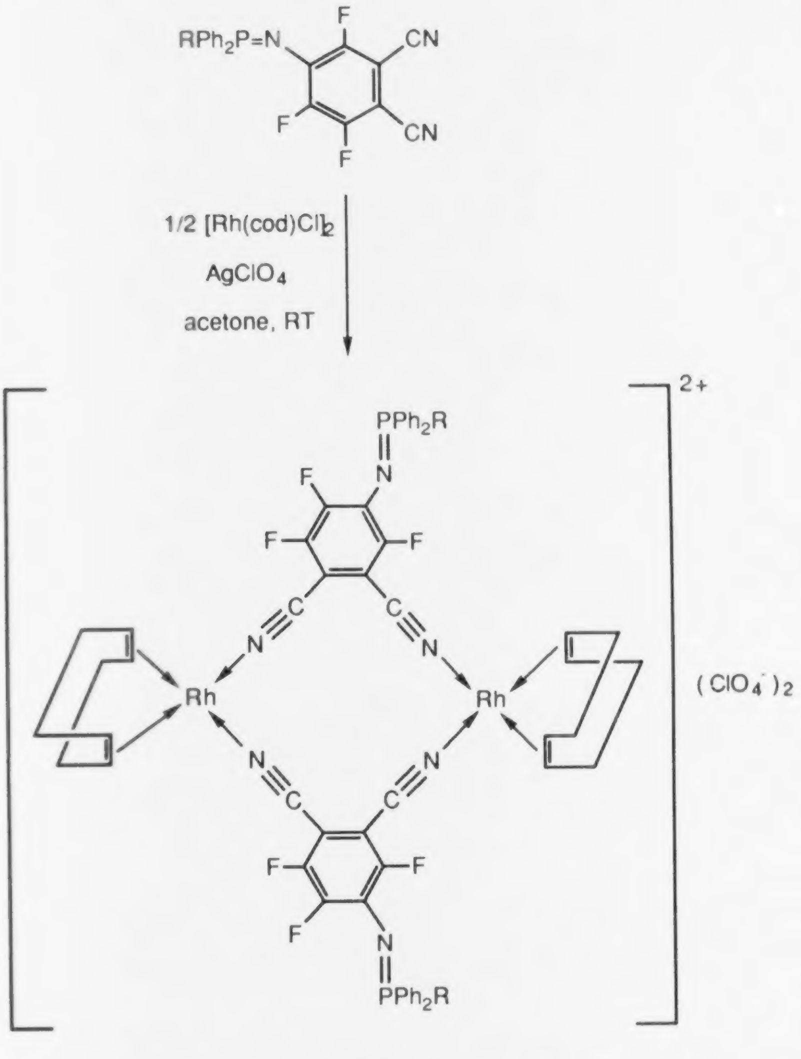

MePh2P=N
F
N=PPh2Me
NC
CN
F
2-2
[Rh(cod)Cl]2
2 AgClO4
acetone, RT
(cod)
Rh
PPh2Me
N
MePh2 P
N
(cod)
Rh
F
F
F
F
N
PPh2Me
Rh
(cod)
MePh2 P
Rh
(cod)
4+
(ClO4)4n
n

2-13

The formulation of (**2-13**) is based on the following evidence: the elemental analysis is consistent with the formula $[LRh_2(cod)_2](ClO_4)_2$. Peaks corresponding to the mass for the ions [(cod)RhLRh(cod)], [RhLRh(cod)], $[L_2Rh(cod)]$, $[L_2Rh]$ and [LRh(cod)] were observed in the mass spectrum (FAB). The ^{31}P NMR showed a broad singlet at 16.39 ppm, which is a downfield shift of about 6.0 ppm compared with the values in the uncoordinated ligand (10.35 ppm). This means that the two phosphinimine groups are chemically equivalent. The ^{19}F NMR spectrum showed two broad peaks at -102.06 and -143.18 ppm respectively. There was no significant difference for the peak at -143.18 ppm compared with the value in the free ligand (-142.31 ppm), but the peak at -102.06 ppm in the complex (assigned to the fluorine between the two CN groups) showed a 5 ppm downfield shift compared with the value for the uncoordinated ligand (-107.06 ppm). The solubility of complex (**2-13**) was poor, and so no solution molecular weight value could be obtained. The IR spectrum showed only one strong band (2238 cm^{-1}) in the region between 1700 and 2700 cm^{-1}, whereas the free ligand showed two bands at 2208 and 2224 cm^{-1}. The CN stretching frequency was higher than either of those for the free ligand (Δ = 14 to 30 cm^{-1}), suggesting that the CN is σ coordinated to the Rh center *via* the lone pair on nitrogen. The geometry of the ligand makes it impossible for the same Rh center to be coordinated with both an imine nitrogen and a CN nitrogen of the same ligand. For this reason, and the demonstrated very poor solubility of the complex, we propose that this compound has a polymeric structure.

Reactions of (**2-6**) and (**2-7**) with $1/2[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C gave complexes, (**2-14**), $[(3,4\text{-}(CN)_2C_6F_3\text{-}N{=}PPh_3)Rh(cod)]_2(ClO_4)_2$, and (**2-15**), $[(3,4\text{-}(CN)_2C_6F_3\text{-}N{=}PPh_2Me)Rh(cod)]_2(ClO_4)_2$, respectively (Equation 2-7). Ions of mass $[L_2Rh(cod)]$ and [LRh(cod)] were observed for (**2-14**) and (**2-15**) in the mass spectra (FAB). The ^{31}P NMR showed signals at 2.0 and 2.8 ppm shifted downfield from the corresponding free ligands, and no significant shift was observed in the ^{19}F NMR spectra. The solution molecular weight for (**2-14**) (918) is about 20% higher than the calculated molecular weight for the monomer, [LRh(cod)](ClO_4). Only one CN band was observed for each complex: 2252 cm^{-1} for (**2-14**), and 2253 cm^{-1} for (**2-15**). This is an increase of 23 cm^{-1} for both (**2-14**) and (**2-15**) compared with the corresponding free ligands (2229 cm^{-1} for (**2-6**) and 2230 cm^{-1} for (**2-7**)). Thus the CN groups are probably coordinated to the Rh center *via* the CN nitrogen lone pair. Since the given ligand geometry does not allow two CN groups to form such bonds to the same Rh center, we propose that this compound is a dimer with σ N→Rh bonds, as illustrated (Equation 2-7).

Equation 2-7:

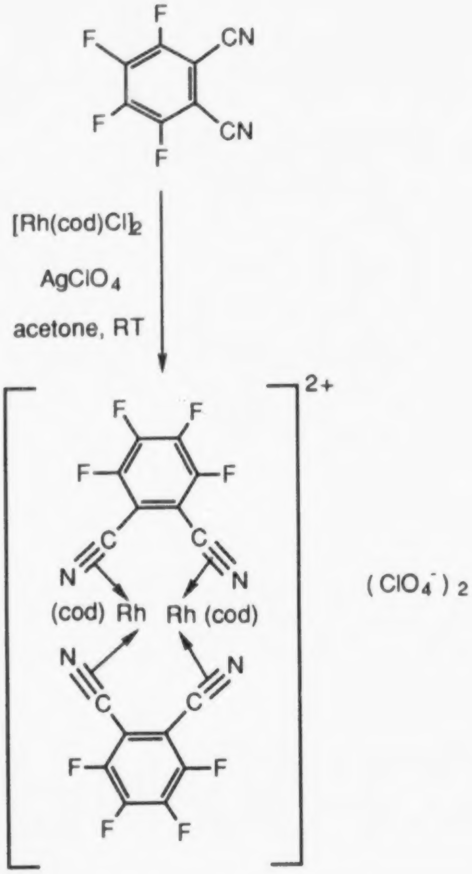

RPh2P=N
F
CN
CN
F
F
1/2 [Rh(cod)Cl]2
AgClO4
acetone, RT
2+
PPh2R
N
F
F
F
C
N
Rh
Rh
(ClO4-)2
PPh2R

2-14 : R = Ph
2-15 : R = Me

The parent fluoroaromatic 1,2-$(CN)_2$-C_6F_4 itself reacted with 1/2$[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C to give complex (**2-16**) (Equation 2-8). The solution molecular weight value (835) is 1.6 times of the molecular weight of monomer,

$[LRh(cod)](ClO_4)$. We therefore propose that the structure of the complex (**2-16**) is also a dimer as illustrated.

Equation 2-8:

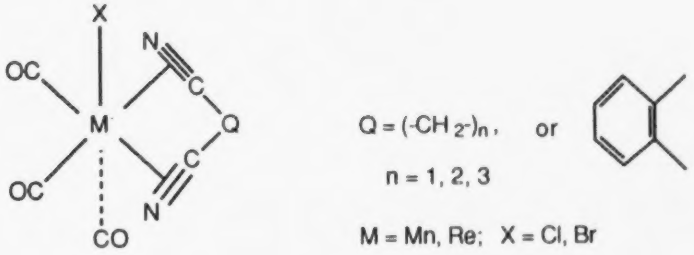

F
F
CN
F
CN
F
$[Rh(cod)Cl]_2$
$AgClO_4$
acetone, RT
F
F
F
F
C
C
N
N
(cod) Rh
Rh (cod)
N
N
C
C
F
F
F
F
2+
$(ClO_4^-)_2$

2-16

The observation of ions of mass $[LRh_2(cod)_2]$, $[L_2Rh]$ and $[LRh(cod)]$ in the mass spectrum (FAB) suggests the proposed dinuclear structure. There was no significant difference in the ^{19}F NMR chemical shift between the ligand, $1,2\text{-}(CN)_2\text{-}C_6F_4$ and the complex. However, the interaction does have a discernable effect on the structure of the spectrum. The ^{19}F NMR spectrum of the ligand shows two signals at

-125.13 ppm and -140.12 ppm, both of which have multiplet structures and are well resolved, exhibiting the typical AA'BB' pattern, expected for the symmetry. In the complex, these signals appear as two broad doublets at -124.27 and -139.20 ppm, both shifted downfield about 1 ppm relative to the free ligand. The CN IR stretching frequency for the complex appears at 2018 cm^{-1}. Compared with the free ligand 1,2-$(CN)_2$-C_6F_4 value of 2246 cm^{-1}, the decrease of 228 cm^{-1} suggests a π coordinated CN ligand.

A previous report[46] suggested a similar structure for bidentate π coordinated nitrile ligands on transition metals, based on large decreases in ν_{CN} similar to those observed herein. One example is the system:



which showed large decreases in ν_{CN} (Δ = -185 cm^{-1} to -230 cm^{-1}) upon coordination compared with the stretching frequencies attributed to the free ligands. In this case, however, it was later argued that the peaks which were assigned by the original author to the CN groups were actually due to CO groups, and that the absorptions due to the CN groups were very weak or undetectable. The complexes were therefore reassigned as σ coordinated dimers.[160,161] For such complexes unambiguous assignment for these IR bands is possible only through isotopic substitution (eg. ^{13}C), because the IR stretching frequencies of CO and CN groups occur in similar regions. Our complexes do not contain CO; thus there is no possibility of this kind of ambiguity. In our case the only reasonable assignment of bands in the 2000 cm^{-1} region is to CN stretching bands, which in some cases show the same very large decreases as have been previously attributed to π-coordinated nitrile ligands.

2.3.3. Molecular Orbital Calculation for Ligand (2-2)

Although it is common for σ-coordinated organonitrile ligands to show an increase in ν_{CN} upon coordination, no reason has been advanced; the only reported analysis concerns calculations of the CN stretching force constants, which show that the increase in frequency corresponds to the increase in the strength of the CN σ-bond.[30,31,162] The reason for the increase in force constant and therefore stretching frequency has not been fully rationalized. We propose that, since the nitrile is isoelectronic with CO, the lone pair in the nitrogen of the nitrile is probably located in an orbital with antibonding character. When RCN is σ-coordinated to metals through nitrogen as the donor, electron density in the antibonding orbital are decreased, and as a result, the bond order is increased, which is reflected in an increase in ν_{CN}. To substantiate this argument, a simple EHMO (Hückel) MO calculation has been performed[163] for (**2-2**) using the molecular parameters obtained from the crystal structure. The results show that the HOMO-2, HOMO-3 and HOMO-4 orbitals for the CN group possess large fractions of the N p_x and p_z characters. The energies of these orbitals are -11.7, -11.9 and -12.0 eV respectively, each of which is higher than the H_{ii} of the free N atom (that is the H_{ii} for N atom in the matrix, which is: 2s orbital = -26 ev, 2p orbitals = -13.4 eV.[164]) Thus, the N atom in the fluoronitrile is a good donor, being more basic than a free N atom. Since the N atom orbitals are out of phase with respect to the adjacent C atoms, the C and N have different coefficient signs. Because the energy of the CN nitrogen is higher than that of free N, the lone pair in the nitrogen has strong antibonding character in the molecule. Consequently ν_{CN} should increase upon σ-coordination to the transition metal.

Table 2-1. Phosphorus-31 NMR[a] Data for Compounds (**1-1**) - (**1-9**).

Compounds[b]		δP^{III} (ppm)	δP^{V} (ppm)	$^{2}J_{PP}$ (Hz)	$^{1}J_{PRh}$ (Hz)
$4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}[N{=}P(Ph)_2CH_2P(Ph)_2)]_2$	**1-1**	-29.5	10.00	49.0	
$4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}[N{=}(PPh)_2CH_2P(Ph)_2]\text{-}3\text{-}(N{=}PPh_3)$	**1-2**	-28.7	10.30 (PPh_2 unit) 8.40 (PPh_3 group)	47.8	
$4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}[N{=}P(Ph)_2CH_2P(Ph)_2]\text{-}3\text{-}(N{=}PPh_2Me)$	**1-3**	-29.2	10.30 (PPh_2 unit) 10.00 (PPh_2Me group)	48.4	
$4,6\text{-}(CN)_2C_6F_2\text{-}3\text{-}(N{=}PPh_3)\text{-}$ $1\text{-}[\overline{N{=}P(Ph)_2CH_2P(Ph)_2Rh}(CO)Cl]$	**1-4**	39.2	44.00(PPh_2 unit) 11.90 (PPh_3 group)	30.9	163.3
$4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}[\overline{N{=}P(Ph)_2CH_2P(Ph)_2Rh}(CO)Cl]_2$	**1-5**	38.8	41.60	32.5	164.9
$4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}[N{=}P(Ph)_2CH_2P(Ph)_2]_2Rh(CO)Cl$	**1-6**	24.2	0.26	1.75 1.85	128.6
$4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}[\overline{N{=}P(Ph)_2CH_2P(Ph)_2Pd}Cl_2]_2$	**1-7**	19.7	50.8	27.5	

Table 2-1. continued

Compounds[b]		$\delta_{P^{III}}$ (ppm)	$\delta_{P^{V}}$ (ppm)	$^{2}J_{PP}$ (Hz)	$^{1}J_{PRh}$ (Hz)
4,6-$(CN)_2C_6F_2$-1,3-$[N{=}P(Ph)_2CH_2P(Ph)_2]_2PdCl_2$	**1-8**	5.8	0.0	*c*	
4,6-$(CN)_2C_6F_2$-1-$[N{=}P(Ph)_2CH_2P(Ph)_2Rh(CO)Cl]$-	**1-9**	16.5 (P-Pd)	48.9 (P-Pd)	29.7 (P-Pd)	
3-$[N{=}P(Ph)_2CH_2P(Ph)_2PdCl_2]$		38.9 (P-Rh)	42.5 (P-Rh)	30.5 (P-Rh)	164.0

[a] Spectra obtained in $CDCl_3$ solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to low field of the standard.

[b] The substituted aromatics are numbered starting from one at the imine attachment point. The numbers associated with the substituents may therefore be different from those used for the systematic name of the original fluroaromatic.

[c] Spectrum is not well resolved.

Table 2-2. ^{31}P NMR[a] Data and the ν_{CN} region IR data of the CN groups for ligands (**2-1**) - (**2-9**).

Compound[b]	**No**	**δP** (ppm)	**ν_{CN}** (cm^{-1})
$4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}(N{=}PPh_3)_2$	**2-1**	8.75	2217
$4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}(N{=}PPh_2Me)_2$	**2-2**	10.03	2208 2224
$4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}(N{=}PPh_3)\text{-}3\text{-}(N{=}PPh_2Me)$	**2-3**	9.30(in PPh_3) 10.20 (in PPh_2Me)	2214
$2,4\text{-}(CN)_2C_6F_3N{=}PPh_3$	**2-4**	13.50	2237
$2,4\text{-}(CN)_2C_6F_3N{=}PPh_2Me$	**2-5**	14.60	2233
$3,4\text{-}(CN)_2C_6F_3\text{-}N{=}PPh_3$	**2-6**	12.60	2229
$3,4\text{-}(CN)_2C_6F_3\text{-}N{=}PPh_2Me$	**2-7**	14.40	2230
$2,5\text{-}(CN)_2C_6F_3\text{-}N{=}PPh_3$	**2-8**	10.81	2230 2240
$2,5\text{-}(CN)_2C_6F_3\text{-}N{=}PPh_2Me$	**2-9**	11.60	2213 2225

[a] Spectra obtained in $CDCl_3$ solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to low field standard.

[b] The imine substituted fluoroaromatics are numbered starting from one at the imine attachment point. The numbers associated with the substituents may therefore be different from those used for the systematic name of the original fluoroaromatic.

Table 2-3. ^{31}P NMR[a] Data and the ν_{CN} region IR[b] data of the CN groups for complexes (**2-10**) - (**2-16**).

Compound[c]	**No**	δ P (ppm)	ν_{CN} (cm^{-1})
$[5\text{-}(CN)\text{-}C_6F_3\text{-}2\text{-}(\pi\text{-}CN)\text{-}1\text{-}(N{=}PPh_3)Rh(cod)](ClO_4)$	**2-10**	13.9(s)	2253 2009
$[5\text{-}(CN)\text{-}C_6F_3\text{-}2\text{-}(\pi\text{-}CN)\text{-}1\text{-}(N{=}PPh_2Me)Rh(cod)](ClO_4)$	**2-11**	17.3(s)[d]	2245 2011
$[4\text{-}(CN)\text{-}C_6F_3\text{-}2\text{-}(\pi\text{-}CN)\text{-}1\text{-}(N{=}PPh_2Me)Rh(cod)](ClO_4)$	**2-12**	20.0(broad)	2253 2055
$[(cod)Rh\text{-}1\text{-}(MePh_2P{=}N\text{-})C_6F_2\text{-}2\text{-}CN\text{-}5\text{-}(N{=}PPh_2Me)\text{-}4\text{-}(CN)Rh(cod)]_n(ClO_4)_{2n}$	**2-13**	16.39(broad)	2238
$[(3,4\text{-}(CN)_2C_6F_3\text{-}1\text{-}(N{=}PPh_3)Rh(cod))_2](ClO_4)_2$	**2-14**	14.6(s)[d]	2252
$[(3,4\text{-}(CN)_2C_6F_3\text{-}1\text{-}(N{=}PPh_2Me)Rh(cod))_2](ClO_4)_2$	**2-15**	17.2(s)[d]	2253
$[(cod)Rh\text{-}1\text{-}(\pi\text{-}CN)\text{-}C_6F_4\text{-}4\text{-}(\pi\text{-}CN)Rh(cod)\text{-}4'\text{-}(\pi\text{-}CN)\text{-}C_6F_4\text{-}1'\text{-}(\pi\text{-}CN)]^{2+}(ClO_4^-)_2$	**2-16**	--------	2018

Table 2-3. continued

[a] Spectra obtained in CD_2Cl_2 solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to low field standard.

[b] The IR samples were obtained as the free crystalline solid using microscope-FTIR instrumentation.

[c] The imine substituted fluoroaromatics are numbered starting from one at the imine attachment point. The numbers associated with the substituents may therefore be different from those used for the systematic name of the original fluoroaromatic.

[d] Spectra obtained in $CDCl_3$ solution.

Table 2-4. Fluorine-19 NMR^a Data and IR^b Data for Compounds (**1-1**) - (**1-9**).

Compound	δ F^c (ppm)	J_{FP} (Hz)	$^5J_{FF}$ (Hz)	ν_{CO} (cm^{-1})	ν_{CN} (cm^{-1})
1-1	F_2: -109.0 (dt) F_1: -140.7 (dt)	$^4J_{F_1\text{-}P^V}=14.0$ $^5J_{F_2\text{-}P^V}=5.0$	11.0		2205
1-2	F_2: -128.9 (a broad doublet) F_1: -138.9 (ddd)	$^4J_{F_1\text{-}P_1}=14.3^d$ $^4J_{F_1\text{-}P_2{}^V}=13.8$ $^5J_{F_2\text{-}P_1}=5.0$ $^5J_{F_2\text{-}P_2{}^V}=4.7$	11.3		2214
1-3	F_2: -108.9 (ddd) F_1: -141.5 (dddd)	$^4J_{F_1\text{-}P_1}=14.6^d$ $^4J_{F_1\text{-}P_2{}^V}=13.9$ $^5J_{F_2\text{-}P_1}=5.0$ $^5J_{F_2\text{-}P_2{}^V}=4.4$ $^4J_{F_1\text{-}P^{III}}=2.6$	11.3		2214
1-4	F_2: -111.6 (dd) F_1: -141.5 (broad)	$^4J_{F_1\text{-}P_1}=6.8^d$ $^4J_{F_1\text{-}P_2{}^V}=11.7$ $^5J_{F_2\text{-}P_1}=6.8$ $^5J_{F_2\text{-}P_2{}^V}=4.8$	11.3	1970	2217

Table 2-4. continued

Compound	δ F^c (ppm)	J_{FP} (Hz)	$^5J_{FF}$ (Hz)	ν_{CO} (cm^{-1})	ν_{CN} (cm^{-1})
1-5	F_2: -106.4 (d) F_1: -119.2 (br. d)		11.3	1977	2227
1-6	F_2: -108.2 (dt) F_1: -136.4 (m)	$^6J_{F_1\text{-}P^{III}}$=3.24 $^5J_{F_1\text{-}P^V}$=8.92 $^5J_{F_2\text{-}P^V}$=5.0	12.0	1972	2216
1-7	F_2: -106.4 (d) F_1: -119.2 (d)		11.9		2228
1-8	F_2: -106.9 (dt) F_1: -137.3 (m)	$^5J_{F_2\text{-}P^V}$=5.3	11.7		2215
1-9	F_2: -107.6 (d) F_1: -121.0 (br. d)		11.7	1979	2228

[a] Spectra obtained in $CDCl_3$ solution; ppm vs $CFCl_3$. Positive values indicate resonance to low field of standard.

[b] The IR samples were run in CH_2Cl_2. [c] F_2 are adjacent to CN groups. [d] P_1 is in the unit PPh_3 or PPh_2Me.

Table 2-5. Summary of Crystallographic Data of Compounds (**1-1**), (**1-2**) and (**1-5**).

compound	**1-1**	**1-2**	**1-5**
formula	$C_{62}H_{50}F_2N_6P_4$	$C_{53}H_{40}F_2N_5P_3$	$C_{62}H_{47}Cl_2F_2N_5O_2P_4Rh_2$
formula weight	1040.96	877.86	1332.71
crystal size (mm)	0.39 × 0.35 × 0.21	0.71 × 0.43 × 0.13	0.27 × 0.23 × 0.15
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n^a$	$C2/c$ (No. 15)
unit cell parameters			
a (Å)	10.6203 (6)	14.101 (2)	25.158 (9)
b (Å)	14.2626 (6)	10.209 (1)	16.379 (2)
c (Å)	20.0527 (8)	31.845 (3)	18.723 (6)
α (deg)	79.577 (4)		
β (deg)	77.371 (4)	99.38 (1)	125.63 (2)
γ(deg)	68.886 (4)		
V (Å^3)	2747.5 (2)	4523 (1)	6271 (7)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.258	1.289	1.412
μ (mm^{-1})	1.686	0.177	0.753

Table 2-5. continued

compound	**1-1**	**1-2**	**1-5**
diffractometer[141]	Siemens P4/RA	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (λ [Å])	Cu Kα (1.54178)	Mo Kα (0.71073)	Mo Kα (0.71073)
temperature (°C)	–60	–50	–50
scan type	θ–2θ	ω	θ–2θ
maximum 2θ (deg)	100.0	50.0	50.0
total data collected	6823	8563	5852
independent reflections (*NR*)	5635	8346	5710
observations (*NO*)	4473[b]	3097[c]	1950[c]
structure solution method	direct methods[d]	direct methods[d]	direct methods[d]
refinement method	full-matrix on F^2[e]	full-matrix on F[f]	full-matrix on F[f]
absorption correction method	*DIFABS*[g]	*DIFABS*[g]	*DIFABS*[g]
range of abs. corr. factors	1.348–0.805	1.084–0.731	1.251–0.764
parameters (*NV*)	667	343	234
goodness-of-fit (*S*)	1.053[h]	1.753[i]	1.549[i]
final *R* indices[j]			
R_1	0.0526[b]	0.064[c]	0.064[c]

Table 2-5. continued

compound	**1-1**	**1-2**	**1-5**
R_2		0.071[c]	0.067[c]
wR_2	0.1426[k]		

[a] A non-standard setting of $P2_1/c$ (No. 14).

[b] $I \geq 2\sigma(I)$.

[c] $I \geq 3\sigma(I)$.

[d] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[e] Sheldrick, G. M. *J. Appl. Cryst.*, in preparation. Refinement on F_o^2 for all reflections (all of these having $F_o^2 < -3\sigma(F_o^2)$). *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on data will be even larger.

[f] *Structure Determination Package*, Version 3 (Enraf-Nonius, Delft, The Netherlands, 1985).

[g] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[h] $S = [\Sigma w_2(F_o^2 - F_c^2)^2/(NR - NV)]^{1/2}$ ($w_2 = [\sigma^2(F_o^2) + (0.0677P)^2 + 2.8559P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[i] $S = [\Sigma w_1(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ ($w_1 = 4F_o^2/\sigma^2(F_o^2)$).

[j] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w_1(|F_o| - |F_c|)^2/\Sigma w_1 F_o^2]^{1/2}$;
$wR_2 = [\Sigma w_2(F_o^2 - F_c^2)^2/\Sigma w_2(F_o^4)]^{1/2}$.

[k] On all data.

Table 2-6. Summary of Crystallographic Data of Compounds (**2-1**), (**2-2**) and (**2-3**).

compound	**2-1**	**2-2**	**2-3**
formula	$C_{44}H_{30}F_2N_4P_2$	$C_{34}H_{26}F_2N_4P_2{\cdot}0.5C_2H_3N$	$C_{42}H_{29}F_2N_4P_2$
formula weight	714.70	611.09	689.67
crystal size (mm)	0.45x0.40x0.10	0.34x0.30x0.16	0.31x0.28x0.22
crystal system	monoclinic	monoclinic	monoclinic
space group^a	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
unit cell parameters			
a (Å)	15.289 (2)	18.694 (2)	9.210 (1)
b (Å)	10.196 (1)	8.576 (1)	18.113 (2)
c (Å)	23.491 (6)	40.084 (4)	20.015 (2)
β (deg)	91.63 (2)	94.00 (1)	100.07 (1)
V (Å^3)	3660 (2)	6411 (2)	3287 (2)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.30	1.27	1.39
μ (cm^{-1})	1.6	1.7	1.76
diffractometer^b	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (λ [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)

Table 2-6. continued

compound	**2-1**	**2-2**	**2-3**
temperature (°C)	21	21	–80
scan type	ω–2θ	ω–2θ	ω–θ
maximum 2θ (deg)	52.0	52.0	52.0
total data collected	4610	6966	7430
independent reflections (*NR*)	4420	6289	6454
observations (*NO*)	2524[c]	3653[c]	3605[c]
structure solution method	direct methods[d]	direct methods[e]	direct methods[d]
refinement method	full-matrix on F[f]	full-matrix on F[f]	full-matrix on F[f]
absorption correction method	*DIFABS*[g]	*DIFABS*[g]	*DIFABS*[g]
range of abs. corr. factors	0.951-0.998	0.916-0.995	0.949-0.999
parameters (*NV*)	237	383	399
goodness-of-fit (*S*)	1.95[h]	1.79[h]	2.34[h]
final *R* indices[i]			
R_1	0.042[j]	0.063[j]	0.056[j]
wR_2	0.051	0.093	0.047

Table 2-6. continued

[a] *a* International Tables

[b] University of Toledo

[c] $Fo^2 > 3.0\sigma(Fo^2)$

[d] MULTAN, Main, Fiske, Hull, Lessinger, Germain, DeClerq & Woolfson, 1980.

[e] SIR, Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989.

[f] *Structure Determination Package*, Version 3 (Enraf-Nonius, Delft, The Netherlands, 1985).

[g] Walker, N.; Stuart, D. *Acta Crystallogr*. **1983**, *A39*, 158.

[h] $S = [\Sigma w_1(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ $(w_1 = 4F_o^2/\sigma^2(F_o^2))$.

[i] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w_1(|F_o| - |F_c|)^2/\Sigma w_1 F_o^2]^{1/2}$;
$wR_2 = [\Sigma w_2(F_o^2 - F_c^2)^2/\Sigma w_2(F_o^4)]^{1/2}$.

[j] $I \geq 3\sigma(I)$

Table 2-7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound (**1-1**).

Atom	x	y	z	U_{eq}, (Å^2)
P1	0.21644(11)	-0.11779(5)	0.34231(5)	0.0360(3)*
P2	0.36381(12)	-0.28224(8)	0.25048(6)	0.0478(3)*
P3	-0.10574(11)	0.16490(8)	0.14201(5)	0.0401(3)*
P4	-0.28006(12)	0.30838(9)	0.24564(6)	0.0478(3)*
F1	0.0489(2)	0.0195(2)	0.24377(11)	0.0449(6))*
F2	-0.3222(3)	-0.1758(2)	0.31058(14)	0.0682(8)*
N1	0.0782(3)	-0.1407(2)	0.3517(2)	0.0397(8)*
N2	-0.1777(3)	0.0843(2)	0.1733(2)	0.0403(9)*
N3	-0.1041(5)	-0.2997(4)	0.4313(3)	0.0781(14)*
N4	-0.4571(5)	0.0110(4)	0.1815(2)	0.089(2)*
C1	-0.0451(4)	-0.0294(3)	0.2612(2)	0.0366(10)*
C2	-0.0245(4)	-0.1074(3)	0.3140(2)	0.0377(10)*
C3	-0.1246(4)	-0.1570(3)	0.3314(2)	0.0399(11)*
C4	-0.2306(4)	-0.1260(3)	0.2944(2)	0.0465(12)*
C5	-0.2486(4)	-0.0473(3)	0.2432(2)	0.0416(11)*
C6	-0.1540(4)	0.0061(3)	0.2239(2)	0.0382(11)*
C7	-0.1128(5)	-0.2368(4)	0.3867(3)	0.0542(13)*
C8	-0.3643(5)	-0.0157(4)	0.2085(2)	0.0572(13)*
C9	0.3336(4)	-0.1499(3)	0.2633(2)	0.0426(11)*
C10	-0.1043(4)	0.2470(3)	0.2001(2)	0.0455(11)*
C11	0.3026(4)	-0.1964(3)	0.4111(2)	0.0388(10)*
C12	0.2489(5)	-0.2641(3)	0.4552(2)	0.0493(12)*
C13	0.3149(5)	-0.3218(4)	0.5089(2)	0.0595(13)*
C14	0.4354(5)	-0.3136(4)	0.5169(2)	0.0572(13)*
C15	0.4898(5)	-0.2476(4)	0.4731(2)	0.0549(13)*
C16	0.4233(4)	-0.1881(3)	0.4203(2)	0.0472(11)*
C21	0.1988(4)	0.0079(3)	0.3556(2)	0.0362(10)*
C22	0.1324(4)	0.0382(3)	0.4199(2)	0.0511(12)*
C23	0.1108(5)	0.1324(4)	0.4363(3)	0.0699(15)*
C24	0.1549(6)	0.1984(4)	0.3894(4)	0.079(2)*
C25	0.2217(6)	0.1727(4)	0.3238(3)	0.072(2)*
C26	0.2441(5)	0.0760(3)	0.3073(2)	0.0539(12)*
C31	0.5042(5)	-0.3019(4)	0.1770(2)	0.0521(12)*
C32	0.5558(5)	-0.2298(4)	0.1377(3)	0.0683(15)*
C33	0.6642(6)	-0.2548(6)	0.0841(3)	0.088(2)*
C34	0.7222(7)	-0.3530(7)	0.0693(3)	0.104(2)*
C35	0.6730(8)	-0.4261(6)	0.1077(3)	0.107(2)*
C36	0.5655(6)	-0.4006(4)	0.1613(3)	0.080(2)*
C41	0.2191(5)	-0.2680(3)	0.2087(2)	0.0461(11)*
C42	0.1469(6)	-0.3335(4)	0.2339(3)	0.0672(14)*
C43	0.0366(7)	-0.3278(5)	0.2045(4)	0.090(2)*
C44	-0.0024(6)	-0.2545(6)	0.1514(3)	0.084(2)*
C45	0.0683(6)	-0.1894(5)	0.1274(3)	0.079(2)*
C46	0.1786(5)	-0.1963(4)	0.1546(2)	0.0600(13)*
C51	0.0648(4)	0.1136(3)	0.0947(2)	0.0393(10)*
C52	0.0752(4)	0.0691(3)	0.0370(2)	0.0484(12)*
C53	0.2003(5)	0.0195(4)	0.0004(3)	0.0653(14)*
C54	0.3177(5)	0.0114(4)	0.0229(3)	0.0704(15)*

Table 2-7. continued

Atom	x	y	z	U_{eq}. (Å^2)
C55	0.3101(5)	0.0571(4)	0.0783(3)	0.0679(15)*
C56	0.1836(5)	0.1089(4)	0.1142(2)	0.0552(13)*
C61	-0.2048(5)	0.2452(3)	0.0780(2)	0.0515(12)*
C62	-0.3223(5)	0.2322(4)	0.0690(3)	0.0667(15)*
C63	-0.3959(7)	0.2936(6)	0.0194(4)	0.096(2)*
C64	-0.3514(9)	0.3678(6)	-0.0210(4)	0.110(3)*
C65	-0.2340(9)	0.3820(4)	-0.0136(3)	0.097(2)*
C66	-0.1583(6)	0.3196(4)	0.0368(2)	0.072(2)*
C71	-0.3009(4)	0.2100(3)	0.3152(2)	0.0460(11)*
C72	-0.2053(5)	0.1588(4)	0.3585(2)	0.0548(13)*
C73	-0.2260(6)	0.0839(4)	0.4081(2)	0.0631(14)*
C74	-0.3420(6)	0.0588(4)	0.4171(3)	0.070(2)*
C75	-0.4389(6)	0.1089(4)	0.3761(3)	0.0720(15)*
C76	-0.4178(5)	0.1838(4)	0.3250(3)	0.0606(13)*
C81	-0.2526(5)	0.3971(3)	0.2915(2)	0.0490(12)*
C82	-0.3700(5)	0.4690(3)	0.3208(2)	0.0576(13)*
C83	-0.3623(7)	0.5426(4)	0.3548(2)	0.068(2)*
C84	-0.3623(7)	0.5426(4)	0.3548(2)	0.068(2)*
C85	-0.1194(6)	0.4749(4)	0.3321(3)	0.076(2)*
C86	-0.1268(6)	0.4002(4)	0.2974(3)	0.0652(14)*

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Anisotropically refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 2-8. Atomic Coordinates and Equivalent Isotropic Displacement parameters for Compound (**1-2**).

Atom	x	y	z	B_{eq}, (Å^2)
P1	0.4410(1)	-0.2090(2)	0.05770(6)	2.99(5)*
P2	0.4192(1)	-0.2175(2)	0.15020(6)	2.33(4)*
P3	0.0206(1)	-0.3918(2)	0.11363(6)	2.62(5)*
F1	0.2249(2)	-0.3148(4)	0.1340(1)	3.1(1)*
F2	0.3438(3)	-0.8188(4)	0.1332(1)	4.2(1)*
N1	0.4253(4)	-0.3725(5)	0.1496(2)	2.7(2)*
N2	0.0875(4)	-0.5166(5)	0.1200(2)	2.6(2)*
N3	0.5618(4)	-0.6620(7)	0.1536(2)	4.9(2)*
N4	0.0963(4)	-0.8596(6)	0.1132(2)	4.7(2)*
C1	0.2554(4)	-0.4431(6)	0.1536(2)	1.9(2)*
C2	0.3543(4)	-0.4626(6)	0.1430(2)	2.2(2)*
C3	0.3819(4)	-0.5972(7)	0.1428(2)	2.3(2)*
C4	0.3137(5)	-0.6913(6)	0.1349(2)	2.6(2)*
C5	0.2160(4)	-0.6698(6)	0.1279(2)	2.3(2)*
C6	0.1845(4)	-0.5364(6)	0.1278(2)	2.2(2)*
C7	0.4829(5)	-0.6311(7)	0.1493(2)	3.3(2)*
C8	0.1493(5)	-0.7738(7)	0.1198(2)	3.0(2)*
C9	0.3769(5)	-0.1410(7)	0.0994(2)	2.5(2)*
C11	0.3745(5)	-0.3607(7)	0.0441(2)	2.7(1)
C12	0.2757(5)	-0.3660(7)	0.0330(2)	3.2(2)
C13	0.2284(5)	-0.4846(8)	0.0247(2)	4.0(2)
C14	0.2787(5)	-0.5986(8)	0.0263(2)	4.3(2)
C15	0.3763(6)	-0.5966(9)	0.0361(3)	5.2(2)
C16	0.4244(5)	-0.4795(8)	0.0452(2)	3.9(2)
C21	0.3891(5)	-0.1091(7)	0.0119(2)	2.9(1)
C22	0.4123(5)	-0.1505(8)	-0.0270(3)	4.6(2)
C23	0.3769(6)	-0.0823(9)	-0.0648(3)	4.9(2)
C24	0.3236(6)	0.0228(9)	-0.0641(3)	5.5(2)
C25	0.2974(7)	0.066(1)	-0.0259(3)	7.0(3)
C26	0.3352(6)	-0.0006(9)	0.0125(3)	5.1(2)
C31	0.5400(4)	-0.1606(6)	0.1645(2)	2.1(1)
C32	0.6178(5)	-0.2449(7)	0.1688(2)	3.6(2)
C33	0.7112(5)	-0.1947(8)	0.1802(2)	3.8(2)
C34	0.7254(5)	-0.0625(8)	0.1859(2)	3.8(2)
C35	0.6489(5)	-0.0241(7)	0.1812(2)	3.4(2)
C36	0.5563(5)	-0.0274(7)	0.1709(2)	3.1(2)
C41	0.3544(4)	-0.1513(6)	0.1896(2)	2.3(1)
C42	0.3832(5)	-0.1985(7)	0.2307(2)	3.2(2)
C43	0.3343(5)	-0.1547(8)	0.2629(2)	4.1(2)
C44	0.2594(5)	-0.0670(8)	0.2536(3)	4.0(2)
C45	0.2318(5)	-0.0216(7)	0.2131(2)	3.4(2)
C46	0.2804(5)	-0.0626(7)	0.1810(2)	2.9(2)
C51	0.0321(4)	-0.2900(7)	0.0685(2)	2.5(1)
C52	0.0817(5)	-0.1714(7)	0.0702(2)	3.1(2)
C53	0.0914(5)	-0.1037(8)	0.0332(2)	4.1(2)
C54	0.0530(5)	-0.1564(8)	-0.0056(3)	4.6(2)
C55	0.0046(6)	-0.2738(8)	-0.0085(2)	4.2(2)
C56	-0.0069(5)	-0.3416(7)	0.0289(2)	3.4(2)

Table 2-8. continued

Atom	x	y	z	U_{eq}, (Å^2)
C61	-0.0992(4)	-0.4569(7)	0.1020(2)	2.7(2)
C62	-0.1778(5)	-0.3736(7)	0.0953(2)	3.5(2)
C63	-0.2706(5)	-0.4229(8)	0.0861(2)	3.7(2)
C64	-0.2837(5)	-0.5553(8)	0.0842(2)	3.9(2)
C65	-0.2078(5)	-0.6402(8)	0.0904(3)	4.5(2)
C66	-0.1140(5)	-0.5909(7)	0.0997(2)	3.5(2)
C71	0.0205(5)	-0.2880(7)	0.1592(2)	3.0(1)
C72	0.0467(5)	-0.3479(8)	0.1989(3)	4.5(2)
C73	0.0384(6)	-0.2733(9)	0.2364(3)	5.8(2)
C74	0.0065(6)	-0.1481(9)	0.2325(3)	5.4(2)
C75	-0.0174(6)	-0.0873(8)	0.1941(3)	4.8(2)
C76	-0.0118(5)	-0.1585(7)	0.1573(2)	3.6(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Anisotropically refined atoms are marked with an asterisk (*). Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, B_{eq}, defined as: $(4/3)\ [a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\ (\cos\gamma)B_{12} + ac\ (\cos\beta)B_{13} + bc\ (\cos\alpha)B_{23}]$.

Table 2-9. Selected Bond Distances[a] (Å) in Compounds (**1-1**), (**1-2**) and (**1-5**).

1-1		**1-2**		**1-5**	
P1-N1	1.581(3)	P1-C9	1.860(5)	Rh-Cl	2.361(4)
P1-C9	1.805(4)	P1-C11	1.826(5)	Rh-P2	2.206(4)
P1-C11	1.802(4)	P1-C21	1.831(6)	Rh-N1	2.153(8)
P1-C21	1.797(4)	P2-N1	1.585(4)	Rh-C6	1.426(3)
P2-C9	1.853(4)	P2-C9	1.807(5)	P1-N1	1.61(1)
P2-C31	1.833(5)	P2-C31	1.787(5)	P1-C7	1.78(1)
P2-C41	1.839(5)	P2-C41	1.802(5)	P1-C11	1.77(1)
P3-N2	1.569(4)	P3-N2	1.578(4)	P1-C21	1.81(1)
P3-C10	1.801(4)	P3-C51	1.803(5)	P2-C7	1.78(1)
P3-C51	1.806(4)	P3-C61	1.797(5)	P2-C31	1.79(1)
P3-C61	1.805(4)	P3-C71	1.798(6)	P2-C41	1.81(1)
P4-C10	1.858(4)	F1-C1	1.377(5)	F1-C1	1.36(2)
P4-C71	1.828(5)	F2-C4	1.373(6)	F2-C4	1.35(2)
P4-C81	1.827(5)	N1-C2	1.351(6)	O-C6	1.12(1)
F1-C1	1.366(4)	N2-C6	1.364(6)	N1-C2	1.40(1)
F2-C4	1.354(5)	N3-C7	1.143(6)	N2-C5	1.12(1)
N1-C6	1.358(5)	N4-C8	1.149(7)	C3-C5	1.46(2)
N2-C2	1.356(5)	C3-C7	1.448(7)		
N3-C8	1.140(6)	C5-C8	1.414(8)		
N4-C7	1.140(6)				
C3-C7	1.429(7)				
C5-C8	1.435(7)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-10. Selected Bond Angles[a] (deg) in Compound (**1-1**).

N1-P1-C11	105.4(2)
N1-P1-C21	115.8(2)
C9-P1-C11	106.4(2)
C9-P1-C21	108.7(2)
C11-P1-C21	103.5(2)
C9-P2-C31	101.3(2)
C9-P2-C41	102.1(2)
C31-P2-C41	100.9(2)
N2-P3-C10	116.4(2)
N2-P3-C51	114.3(2)
N2-P3-C61	105.0(2)
C10-P3-C51	109.2(2)
C10-P3-C61	106.3(2)
C51-P3-C61	104.5(2)
C10-P4-C71	102.0(2)
C10-P4-C81	101.6(2)
C71-P4-C81	101.7(2)
P1-N1-C6	132.1(3)
P3-N2-C2	133.2(3)
F1-C1-C2	116.8(3)
F1-C1-C6	116.3(3)
N1-C2-C1	127.5(4)
N1-C2-C3	116.8(4)
F2-C4-C5	118.6(4)
F2-C4-C3	117.9(4)
N2-C6-C1	127.5(4)
N2-C6-C5	118.0(4)
N3-C7-C3	179.2(5)
N4-C8-C5	178.8(5)
P1-C9-P2	110.2(2)
P3-C10-P4	110.7(2)
P1-C11-C12	121.0(3)
P1-C11-C16	119.6(3)
P1-C21-C22	116.4(3)
P1-C21-C26	125.4(3)
P2-C31-C32	127.0(4)
P2-C31-C36	115.3(4)
P2-C41-C42	117.2(4)
P2-C41-C46	124.4(4)
P3-C51-C56	125.4(3)
P3-C51-C52	116.1(3)
P3-C61-C62	121.1(4)
P3-C61-C66	118.4(4)
P4-C71-C76	118.3(4)
P4-C71-C72	123.8(4)
P4-C81-C86	125.8(4)
P4-C81-C82	115.8(4)
C2-C3-C7	119.3(4)
C4-C3-C7	121.8(4)
C4-C5-C8	121.0(4)
C6-C5-C8	118.6(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-11. Selected Bond Angles[a] (deg) in Compound (**1-2**).

C9-P1-C11	101.3(2)
C9-P1-C21	100.6(2)
C11-P1-C21	99.2(2)
N1-P2-C9	115.5(3)
N1-P2-C31	106.1(3)
N1-P2-C41	114.7(3)
C9-P2-C31	104.5(2)
C9-P2-C41	109.3(2)
C31-P2-C41	105.7(2)
N2-P3-C51	116.0(2)
N2-P3-C61	104.5(3)
N2-P3-C71	116.8(3)
C51-P3-C61	104.7(2)
C51-P3-C71	108.5(3)
C61-P3-C71	105.0(3)
P2-N1-C2	129.9(4)
P3-N2-C6	134.7(4)
F1-C1-C2	116.2(5)
F1-C1-C6	116.1(4)
N1-C2-C1	128.8(5)
N1-C2-C3	117.4(5)
F2-C4-C3	117.8(5)
F2-C4-C5	116.9(5)
N2-C6-C1	127.4(5)
N2-C6-C5	116.3(5)
N3-C7-C3	177.6(7)
N4-C8-C5	178.9(7)
P1-C9-P2	110.5(3)
P1-C11-C12	123.4(4)
P1-C11-C16	119.5(4)
P1-C21-C22	114.6(5)
P1-C21-C26	126.9(5)
P2-C31-C32	122.0(4)
P2-C31-C36	118.9(4)
P2-C41-C42	114.9(4)
P2-C41-C46	124.2(4)
P3-C51-C52	125.4(4)
P3-C51-C56	115.5(4)
P3-C61-C62	120.4(4)
P3-C61-C66	120.3(4)
P3-C71-C72	115.9(5)
P3-C71-C76	124.4(5)
C2-C3-C7	119.5(5)
C4-C3-C7	120.6(5)
C4-C5-C8	121.9(5)
C6-C5-C8	121.1(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-12. Table of Positional Parameters and Their Estimated Standard Deviations[a] for (**2-1**).

Atom	x	y	z	B (Å^2)
P1	0.05652(4)	0.22559(6)	0.37178(2)	2.81(1)
F1	0.000	0.2168(2)	0.250	3.55(4)
F2	0.000	-0.3146(2)	0.250	5.03(5)
N1	0.0528(1)	0.0791(2)	0.35007(8)	3.28(4)
N2	0.0811(2)	-0.2482(2)	0.3874(1)	5.83(6)
C1	0.0265(1)	0.0215(2)	0.30063(9)	2.82(4)
C2	0.000	0.0823(3)	0.250	2.74(6)
C3	0.0265(1)	-0.1191(2)	0.2994(1)	3.18(5)
C4	0.000	-0.1820(3)	0.250	3.44(7)
C5	0.0559(2)	-0.1903(2)	0.3485(1)	4.01(5)
C6	0.1404(1)	0.3221(2)	0.33905(9)	2.88(4)
C7	0.1551(2)	0.4526(2)	0.3528(1)	4.11(5)
C8	0.2270(2)	0.5174(3)	0.3312(1)	5.03(6)
C9	0.2827(2)	0.4536(3)	0.2960(1)	4.95(6)
C10	0.2676(2)	0.3254(3)	0.2814(1)	4.58(6)
C11	0.1967(1)	0.2602(2)	0.3206(1)	3.59(5)
C12	0.0878(1)	0.2160(2)	0.4460(1)	3.54(5)
C13	0.0828(2)	0.3258(3)	0.4802(1)	5.85(7)
C14	0.1113(2)	0.3209(4)	0.5364(1)	7.51(9)
C15	0.1442(2)	0.2090(4)	0.5585(1)	7.8(1)
C16	0.1494(3)	0.0995(4)	0.5256(1)	8.3(1)
C17	0.1203(2)	0.1015(3)	0.4688(1)	5.98(7)
C18	-0.0450(1)	0.3159(2)	0.36868(9)	3.03(4)
C19	-0.0616(2)	0.4183(2)	0.3313(1)	3.88(5)
C20	-0.1423(2)	0.4788(3)	0.3291(1)	4.77(6)
C21	-0.2070(2)	0.4373(3)	0.3638(1)	5.30(7)
C22	-0.1919(2)	0.3365(3)	0.4008(1)	5.69(7)
C23	-0.1110(2)	0.2760(3)	0.4042(1)	4.71(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-13. Table of Positional Parameters and Their Estimated Standard Deviations[a,b] for (**2-2**).

Atom	x	y	z	B_{eq}, (Å^2)
P1	0.59645(5)	0.4121(1)	0.67608(3)	3.71(2)
P2	0.44979(5)	0.3583(1)	0.54557(3)	3.49(2)
F1	0.5300(1)	0.3837(3)	0.60939(6)	5.23(6)
F2	0.7652(1)	0.1143(3)	0.56337(6)	4.91(5)
N1	0.6496(2)	0.3228(4)	0.65418(8)	4.30(8)
N2	0.5289(2)	0.2974(4)	0.54138(8)	3.97(7)
N3	0.6565(2)	0.1493(5)	0.48977(9)	5.60(9)
N4	0.8181(2)	0.1546(5)	0.64713(9)	5.23(9)
N5	0.1230(5)	0.500(1)	0.2905(4)	13.2(4)*
C1	0.6418(2)	0.4239(5)	0.7174(1)	4.17(9)
C2	0.7006(3)	0.3369(7)	0.7255(1)	6.9(1)
C3	0.7347(4)	0.3439(9)	0.7577(1)	8.7(2)
C4	0.7066(3)	0.4372(7)	0.7815(1)	6.9(1)
C5	0.6473(3)	0.5246(7)	0.7728(1)	6.3(1)
C6	0.6147(3)	0.5181(6)	0.7413(1)	5.3(1)
C7	0.5771(2)	0.6099(5)	0.6632(1)	4.04(9)
C8	0.6330(3)	0.7060(6)	0.6576(1)	6.3(1)
C9	0.6213(3)	0.8553(7)	0.6459(2)	8.0(2)
C10	0.5539(3)	0.9105(7)	0.6404(2)	7.8(2)
C11	0.4966(3)	0.8162(7)	0.6453(2)	7.8(2)
C12	0.5076(2)	0.6641(6)	0.6569(1)	5.8(1)
C13	0.5135(2)	0.3150(6)	0.6826(1)	5.6(1)
C14	0.6465(2)	0.2894(5)	0.6276(9)	3.14(7)
C15	0.5893(2)	0.3154(5)	0.59777(9)	3.43(8)
C16	0.5853(2)	0.2780(5)	0.56386(9)	3.26(8)
C17	0.6494(2)	0.2115(5)	0.55205(9)	3.30(7)
C18	0.6527(2)	0.1761(5)	0.5175(1)	3.92(9)
C19	0.7061(2)	0.1825(5)	0.57446(9)	3.44(8)
C20	0.7073(2)	0.2169(5)	0.60827(9)	3.23(7)
C21	0.7685(2)	0.1823(5)	0.63001(9)	3.64(8)
C22	0.4007(2)	0.2535(5)	0.57565(9)	3.49(8)
C23	0.3705(2)	0.3247(6)	0.6024(1)	4.42(9)
C24	0.3329(2)	0.2374(6)	0.6241(1)	5.3(1)
C25	0.3244(3)	0.0767(6)	0.6193(1)	5.4(1)
C26	0.3539(3)	0.0093(6)	0.5932(1)	5.3(1)
C27	0.3922(2)	0.0940(5)	0.5711(1)	4.32(9)
C28	0.4021(2)	0.3232(5)	0.50558(9)	3.86(8)
C29	0.4286(2)	0.2189(6)	0.4836(1)	4.8(1)
C30	0.3923(3)	0.1926(7)	0.4530(1)	6.1(1)
C31	0.3287(3)	0.2728(8)	0.4447(1)	7.4(1)
C32	0.3015(3)	0.3752(8)	0.4668(1)	7.4(1)
C33	0.3386(2)	0.3991(7)	0.4972(1)	5.8(1)
C34	0.4426(2)	0.5618(5)	0.5538(1)	4.9(1)
C35	0.097	0.505	0.263	13.2*
C36	0.064	0.511	0.230	13.2*

Numbers in parentheses are estimated standard deviations in the least significant digits. Starred atoms were refined as riding atoms with U = 1.3 x Uequiv of atom upon which it rides.

Table 2-14. Table of Positional Parameters and Their Estimated Standard Deviations for (**2-3**).

Atom	x	y	z	B_{eq}, (Å^2)
P1	0.0431(1)	0.17153(6)	0.48570(5)	2.28(2)
P2	-0.5353(1)	0.20624(7)	0.31003(5)	3.10(2)
F1	-0.2516(2)	0.1887(1)	0.3888(1)	3.90(6)
F2	-0.0641(3)	0.0133(1)	0.2025(1)	3.99(6)
N1	0.0300(3)	0.1258(2)	0.4185(2)	2.74(7)
N2	-0.4473(3)	0.1545(2)	0.2672(2)	3.48(8)
N3	0.2471(4)	0.0199(2)	0.3296(2)	4.26(9)
N4	-0.4052(4)	0.0642(2)	0.1151(2)	4.4(1)
C1	-0.0639(4)	0.1147(2)	0.3595(2)	2.40(8)
C2	-0.2066(4)	0.1431(2)	0.3422(2)	2.61(9)
C3	-0.3067(4)	0.1296(2)	0.2825(2)	2.69(9)
C4	-0.2528(4)	0.0845(2)	0.2343(2)	2.55(9)
C5	-0.1134(4)	0.0559(2)	0.2494(2)	2.70(9)
C6	-0.0183(4)	0.0689(2)	0.3097(2)	2.47(9)
C7	-0.3407(4)	0.0725(2)	0.1685(2)	3.1(1)
C8	0.1291(4)	0.0408(2)	0.3212(2)	2.93(9)
C9	-0.5666(4)	0.1727(2)	0.3907(2)	3.5(1)
C10	-0.4596(4)	0.2982(3)	0.3232(2)	3.7(1)
C11	-0.3820(5)	0.3251(3)	0.2739(3)	5.1(1)*
C12	-0.3201(6)	0.3955(3)	0.2844(3)	6.9(1)*
C13	-0.3323(6)	0.4341(4)	0.3382(3)	7.3(2)*
C14	-0.4041(6)	0.4108(3)	0.3890(3)	7.3(2)*
C15	-0.4719(5)	0.3399(3)	0.3799(3)	5.2(1)*
C16	-0.7181(4)	0.2136(3)	0.2600(2)	3.5(1)
C17	-0.7624(5)	0.1689(2)	0.2048(2)	4.1(1)
C18	-0.9084(5)	0.1718(3)	0.1708(2)	5.1(1)
C19	-0.10064(4)	0.2190(3)	0.1931(2)	5.4(1)
C20	-0.9622(5)	0.2648(3)	0.2478(2)	5.7(1)
C21	-0.8174(4)	0.2624(3)	0.2814(2)	4.6(1)
C25	0.1116(4)	0.2640(2)	0.4761(2)	2.54(9)
C26	0.0370(5)	0.3086(3)	0.4248(2)	3.9(1)
C27	0.0830(5)	0.3802(3)	0.4168(2)	5.1(1)
C28	0.2044(5)	0.4077(3)	0.4590(3)	5.1(1)
C29	0.2806(5)	0.3641(3)	0.5097(2)	4.4(1)
C30	0.2344(4)	0.2924(2)	0.5188(2)	3.1(1)
C31	0.1749(4)	0.1217(2)	0.5464(2)	2.30(8)
C32	0.2579(5)	0.0666(2)	0.5241(2)	2.95(9)
C33	0.3562(5)	0.0262(2)	0.5701(2)	3.6(1)
C34	0.3728(4)	0.0406(2)	0.6384(2)	3.3(1)
C35	0.2907(4)	0.0950(2)	0.6612(2)	3.4(1)
C36	0.1918(4)	0.1355(2)	0.6154(2)	3.01(9)
C37	-0.1174(4)	0.1838(2)	0.5256(2)	2.40(8)
C38	-0.1749(4)	0.1221(3)	0.5522(2)	3.9(1)
C39	-0.3031(5)	0.1269(3)	0.5796(2)	5.5(1)
C40	-0.3733(5)	0.1943(3)	0.5795(2)	5.0(1)
C41	-0.3186(4)	0.2558(3)	0.5537(2)	4.1(1)
C42	-0.1895(4)	0.2510(2)	0.5263(2)	2.96(9)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-14. continued

Starred atoms were refined as riding atoms with U = 1.3 x Uequiv of atom which it rides.

Table 2-15. Selected Bond Distances[a] (Å) in the compounds (**2-1**), (**2-2**) and (**2-3**).

2-1		**2-2**		**2-3**	
Distances:					
P(1)-N(1)	1.579(2)	P(1)-N(1)	1.570(4)	P(1)-N(1)	1.567(4)
N(1)-C(1)	1.352(3)	P(2)-N(2)	1.589(3)	P(2)-N(2)	1.581(5)
N(2)-C(5)	1.146(4)	N(1)-C(14)	1.367(5)	N(1)-C(1)	1.350(6)
C(3)-C(5)	1.426(3)	N(2)-C(16)	1.348(4)	N(2)-C(3)	1.359(6)
		N(3)-C(18)	1.140(5)	N(3)-C(8)	1.134(6)
		N(4)-C(21)	1.139(5)	N(4)-C(7)	1.135(6)
		N(5)-C(35)	1.16(1)	C(6)-C(8)	1.435(7)
		C(17)-C(18)	1.425(5)	C(4)-C(7)	1.439(7)
		C(20)-C(21)	1.420(5)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-16. Selected Bond Angles (deg) in the compound (**2-1**).

Atoms	Angles
P(1)-N(1)-C(1)	134.0(2)
N(1)-P(1)-C(6)	113.5(1)
N(1)-P(1)-C(12)	105.5(1)
N(1)-P(1)-C(18)	116.5(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-17. Selected Bond Angles (deg) in the compounds (**2-2**) and (**2-3**).

2-2		**2-3**	
Atoms	Angles	Atoms	Angles
P(1)-N(1)-C(14)	131.6(3)	P(1)-N(1)-C(1)	140.4(4)
P(2)-N(2)-C(16)	131.3(3)	P(2)-N(2)-C(3)	129.4(4)
N(1)-P(1)-C(1)	105.3(2)	N(1)-P(1)-C(25)	112.0(2)
N(1)-P(1)-C(7)	114.9(2)	N(1)-P(1)-C(31)	104.8(2)
N(1)-P(1)-C(13)	116.2(2)	N(1)-P(1)-C(37)	119.7(2)
N(2)-P(2)-C(22)	115.3(2)	N(2)-P(2)-C(9)	117.8(3)
N(2)-P(2)-C(28)	104.9(2)	N(2)-P(2)-C(10)	113.7(3)
N(2)-P(2)-C(34)	115.1(2)	N(2)-P(2)-C(16)	104.9(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-18. Least-Squares Planes and Dihedral Angles (deg) in Compound (**1-1**).

Plane	Coefficients[a]				Defining Atoms with Deviations(Å)[b]			
1	-2.026(17)	8.626(18)	13.681(22)	3.420(7)	C1	-0.009(3)	C2	0.000(3)
					C3	0.011(3)	C4	-0.012(3)
					C5	0.003(3)	C6	0.008(3)
					P1	-0.191(7)	P3	0.160(6)
					F1	-0.016(5)	F2	-0.035(6)
					N1	0.020(6)	N2	0.038(5)
					N3	0.107(8)	N4	0.083(8)
					C7	0.056(7)	C8	0.035(7)
2	-1.595(18)	9.695(19)	12.712(26)	2.838(16)	C11	0.001(3)	C12	-0.008(3)
					C13	0.010(4)	C14	-0.002(3)
					C15	-0.006(3)	C16	0.006(3)
3	2.878(20)	8.049(26)	13.016(30)	0.072(10)	C41	-0.001(3)	C42	-0.009(4)
					C43	0.010(4)	C44	-0.001(4)
					C45	-0.009(4)	C46	0.010(3)
4	-1.958(23)	8.701(24)	13.684(29)	3.598(5)	C61	0.005(3)	C62	-0.002(3)
					C63	-0.003(4)	C64	0.004(5)
					C65	-0.001(4)	C66	-0.003(4)
5	-0.999(20)	9.587(19)	13.826(25)	6.676(7)	C71	-0.004(3)	C72	0.008(3)
					C73	-0.004(3)	C74	-0.003(3)
					C75	0.006(4)	C76	-0.003(3)

Table 2-18. continued

Dihedral Angles (deg)							
Planes	Angle	Planes	Angle	Planes	Angle	Planes	Angle
1-2	5.79(26)	1-3	4.73(31)	1-4	0.42(30)	1-5	5.98(26)
2-3	8.73(31)	2-4	5.47(31)	2-5	4.57(28)	3-4	5.10(34)
3-5	10.51(30)	4-5	5.57(31)				

[a] Coefficients are for the form ax+by+cz-d=0 where x,y and z are crystallographic coordinates.

[b] Underlined atoms were not included in the definition of the plane.

Table 2-19. Weighted[a] Least-Squares Planes and Dihedral Angles (deg) in Compound (**1-2**).

Plane	Coefficients[b]				Defining Atoms with Deviations(Å)			
1	2.5750	0.6566	-31.7729	-3.9397	C1	-0.003	C2	0.004
					C3	-0.007	C4	0.009
					C5	-0.006	C6	0.003
2	3.2953	1.0185	-31.6014	-0.5170	C11	-0.009	C12	0.011
					C13	-0.004	C14	-0.006
					C15	0.009	C16	-0.001

Dihedral Angles (deg)

Planes	Angle
1-2	3.7

[a] Weights are derived from the atomic positional e. s. d.'s using the method of Hamilton (Hamilton, W.C. Acta Crystallogr. 1961, 14, 185).

[b] Coefficients are for the form ax+by+cz-d=0 where x, y and z are crystallographic coordinates.

Table 2-20. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound (**1-5**).

Atom	x	y	z	B_{eq}, (Å^2)
Rh	0.15478(5)	0.33459(8)	0.22641(6)	1.97(2)*
Cl	0.1749(1)	0.3851(3)	0.3852(2)	3.2(1)*
P1	0.0153(1)	0.2591(2)	0.1038(2)	2.1(1)*
P2	0.1283(1)	0.2811(3)	0.1015(2)	2.3(1)*
F1	0	0.2515(7)	0.25	2.3(3)*
F2	0	0.5809(7)	0.25	3.4(3)*
O	0.2922(4)	0.3380(8)	0.2869(6)	4.8(4)*
N1	0.0524(4)	0.3327(8)	0.1728(5)	2.1(3)*
N2	0.0619(5)	0.5416(9)	0.1293(7)	5.0(5)*
C1	0	0.334(1)	0.25	1.4(3)*
C2	0.0261(5)	0.3735(8)	0.2113(7)	2.0(4)*
C3	0.0254(5)	0.4588(8)	0.2110(7)	1.9(4)*
C4	0	0.498(1)	0.25	2.1(6)*
C5	0.0480(5)	0.5054(9)	0.1670(8)	2.7(4)*
C6	0.2400(5)	0.338(1)	0.2648(8)	3.6(5)*
C7	0.0413(6)	0.2728(9)	0.0344(7)	2.5(4)*
C11	-0.0711(5)	0.2655(8)	0.0425(7)	1.7(3)
C12	-0.1029(5)	0.331(1)	-0.0149(8)	3.1(3)
C13	-0.1691(6)	0.341(1)	-0.0620(8)	3.7(3)
C14	-0.2038(7)	0.282(1)	-0.0552(9)	4.8(4)
C15	-0.1749(6)	0.217(1)	-0.0015(8)	3.5(4)
C16	-0.1085(6)	0.209(1)	0.0470(8)	3.4(4)
C21	0.0423(5)	0.158(1)	0.1509(7)	2.4(3)
C22	0.0618(7)	0.091(1)	0.097(1)	5.1(4)
C23	0.0932(7)	0.016(1)	0.134(1)	5.3(5)
C24	0.0874(7)	0.005(1)	0.217(1)	6.1(5)
C25	0.1130(7)	0.073(1)	0.2725(9)	4.8(4)
C26	0.0887(6)	0.148(1)	0.2369(8)	3.3(3)
C31	0.1516(5)	0.338(1)	0.0423(7)	2.1(3)
C32	0.2055(6)	0.317(1)	0.0459(9)	4.4(4)
C33	0.2294(6)	0.368(1)	0.0116(9)	4.1(4)
C34	0.1989(6)	0.437(1)	-0.0314(8)	3.9(4)
C35	0.1462(6)	0.459(1)	-0.0337(9)	4.1(4)
C36	0.1220(6)	0.410(1)	0.0007(8)	3.3(4)
C41	0.1537(5)	0.1784(9)	0.0988(7)	2.6(3)
C42	0.1266(6)	0.1360(9)	0.0239(8)	3.2(4)
C43	0.1461(6)	0.057(1)	0.0239(9)	4.1(4)
C44	0.1916(7)	0.020(1)	0.0970(9)	4.8(4)
C45	0.2213(6)	0.059(1)	0.1745(9)	3.9(4)
C46	0.2020(6)	0.140(1)	0.1765(8)	3.5(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Anisotropically refined atoms are marked with an asterisk (*). Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, B_{eq}, defined as: $(4/3)\ [a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. Those parameters without an e. s. d. were not refined.

Table 2-21. Selected Bond Angles[a] (deg) in Compound (**1-5**).

Cl-Rh-P2	174.7(1)	Rh-N1-C2	123.4(8)
Cl-Rh-N1	87.8(3)	P1-N1-C2	123.0(8)
Cl-Rh-C6	95.2(4)	F1-C1-C2	117.6(9)
P2-Rh-N1	87.7(3)	N1-C2-C1	124(1)
P2-Rh-C6	89.4(4)	N1-C2-C3	119(1)
N1-Rh-C6	176.4(5)	C2-C3-C5	121(1)
N1-P1-C7	101.8(5)	C4-C3-C5	121(1)
N1-P1-C11	113.2(5)	F2-C4-C3	117.9(8)
N1-P1-C21	114.6(6)	N2-C5-C3	176(2)
C7-P1-C11	110.7(6)	Rh-C6-O	178(1)
C7-P1-C21	106.2(5)	P1-C7-P2	108.5(6)
C11-P1-C21	109.9(5)	P1-C11-C12	118.9(9)
Rh-P2-C7	105.4(4)	P1-C11-C16	124(1)
Rh-P2-C31	116.4(4)	P1-C21-C22	119(1)
Rh-P2-C41	120.3(4)	P1-C21-C26	121(1)
C7-P2-C31	108.3(5)	P2-C31-C32	121(1)
C7-P2-C41	102.6(6)	P2-C31-C36	122.3(9)
C31-P2-C41	102.6(6)	P2-C41-C42	123(1)
Rh-N1-P1	111.2(5)	P2-C41-C46	120(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2-22. Weighted[a] Least-Squares Planes and Dihedral Angles (deg) in Compound (**1-5**).

Plane	Coefficients[b]				Defining Atoms with Deviations(Å)[c]			
1	-2.8616	-15.1944	6.6518	-4.0117	Cl	0.043	P2	0.049
					N1	-0.044	C6	-0.048
					$\underline{\mathrm{Rh}}$	-0.009	$\underline{\mathrm{P1}}$	0.722
					$\underline{\mathrm{O}}$	-0.052	$\underline{\mathrm{C7}}$	-0.023
					$\underline{\mathrm{C2}}$	-0.226		
2	12.0642	0.0407	8.1248	2.0465	N1	0.003	C1	-0.002
					C2	0.000	C3	-0.007
					C4	0.005		
					$\underline{\mathrm{F1}}$	-0.005	$\underline{\mathrm{F2}}$	0.008
					$\underline{\mathrm{N2}}$	-0.226	$\underline{\mathrm{C5}}$	-0.090
3	-3.6279	-15.1156	7.0062	-4.0195	Rh	-0.013	P2	0.016
					N1	0.011	C7	-0.014
4	-13.5740	9.7821	-3.1471	1.9999	C7	P1	N1	

Dihedral Angles (deg)

Planes	Angle	Planes	Angle	Planes	Angle
1-2	75.2	1-3	1.8	1-4	134.7
2-3	76.0	2-4	141.1	3-4	133.3

[a] Weights are derived from the atomic positional e. s. d.'s using the method of Hamilton (Hamilton, W.C. Acta Crystallogr. 1961, 14, 185).

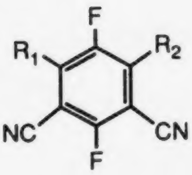
[b] Coefficients are for the form ax+by+cz-d=0 where x,y and z are crystallographic coordinates.

[c] Underlined atoms were not included in the definition of the plane.

Table 2-23. Parameters (coupling constants of ^{31}P NMR) Used in the Simulation for Compound (**1-6**).

	Coupling Constants (Hz)
${}^1J_{P(A)\text{-}Rh} = {}^1J_{P(A')\text{-}Rh}$	128.5
${}^2J_{P(A)\text{-}P(B)} = {}^2J_{P(A')\text{-}P(B')}$	1.85
${}^4J_{P(A)\text{-}P(B')} = {}^4J_{P(A')\text{-}P(B)}$	1.75
${}^6J_{P(A)\text{-}F(A)} = {}^6J_{P(A')\text{-}F(A)}$	3.24
${}^4J_{P(B)\text{-}F(A)} = {}^4J_{P(B')\text{-}F(A)}$	8.92
${}^5J_{P(B)\text{-}F(B)} = {}^5J_{P(B')\text{-}F(B)}$	5.00
${}^5J_{F(A)\text{-}F(B)}$	12.00

Table 2-24. Shifts in ν_{CN} on Substitution.



R_1 / R_2	ν_{CN} (cm^{-1})	$\Delta(cm^{-1})^a$
F / F	2252	
F / N=PPh_3	2237	15
F / N=$P(Ph)_2CH_2PPh_2$	2231	21
N=PPh_3 / N=PPh_3	2217	35
N=PPh_3 / N=$P(Ph)_2CH_2PPh_2$	2214	38
N=$P(Ph)_2CH_2PPh_2$ / N=$P(Ph)_2CH_2PPh_2$	2205	47

[a] $\Delta = (2252 - \nu_{CN})\ cm^{-1}$.

Chapter 3

New Phosphinimine Substituted Ligands Formed from Halogenated *p*-Benzoquinones, and Their Cationic Rhodium(I) Complexes

3.1. Mono and Bis-phosphinimine Substituted *p*-Fluoro- or *p*-Chlorobenzoquinone Derivatives and Their Cationic Rh(I) Complexes

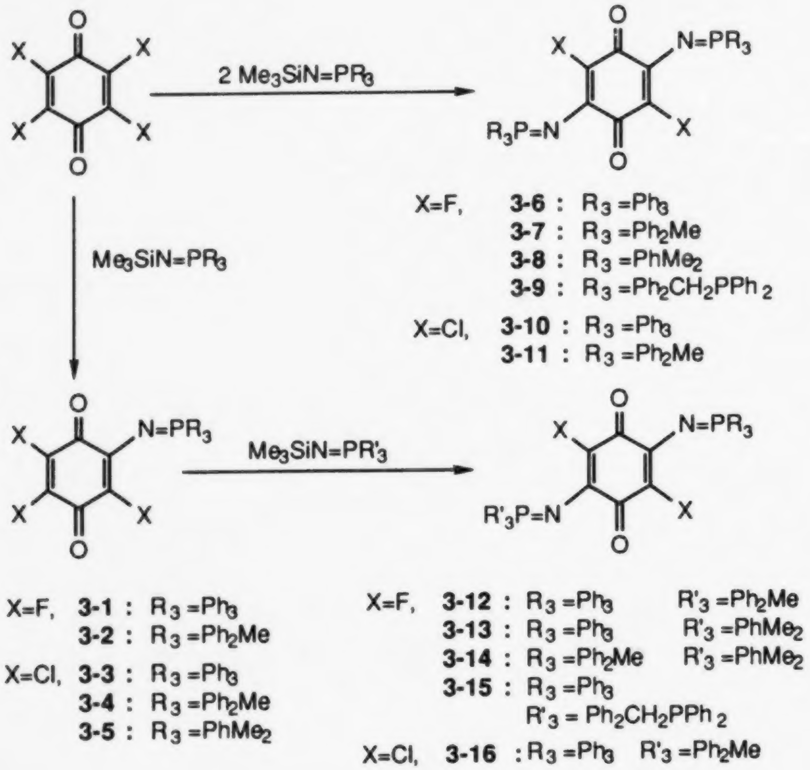
3.1.1. Synthesis and Properties of the Ligands

The reaction of tetrafluoro- and tetrachloro-*p*-benzoquinone with one or two equivalents of a series of trimethylsilyl phosphinimines in CH_2Cl_2 gave a series of the corresponding mono- or disubstituted *p*-benzoquinone derivatives **(3-1)** - **(3-11)** in good yields. These reactions could be conducted either using a 1:2 ratio to proceed directly to the equivalently disubstituted products **(3-6)** - **(3-11)** or stepwise using an initial 1:1 ratio to form the monosubstituted products **(3-1)** - **(3-5)**. The monosubstituted derivatives can then be reacted with another equivalent of a different trimethylsilyl phosphinimine to form the derivatives containing two dissimilar phosphinimine substituents, **(3-12)** - **(3-16)** (Scheme 3-1).

The mono- and disubstituted compounds are each air-stable solids and are soluble in most common organic solvents. Each monosubstituted derivative is strongly colored purple or blue, and the disubstituted derivatives are green. Each of the mono- and disubstituted derivatives has a high UV-visible molar extinction coefficient, with higher values being demonstrated by the disubstituted compounds (Table 3-1).

The composition and structure of each of the compounds has been determined from the analytical data, mass spectra and ^1H, ^{31}P and ^{19}F NMR spectroscopy. Molecular ions for each of the compounds have been observed in the mass spectra. Phosphorus-31 NMR data are given in Table 3-1. The presence of one signal for the P^{III} and P^{V} centers in the ^{31}P NMR of compound **(3-9)** show that the two PCPN groups are chemically equivalent. However, when different imine phosphorus substituents are present in the same molecule, the different P^{III} and P^{V} moities are readily distinguished by their different chemical shifts.

Scheme 3-1:



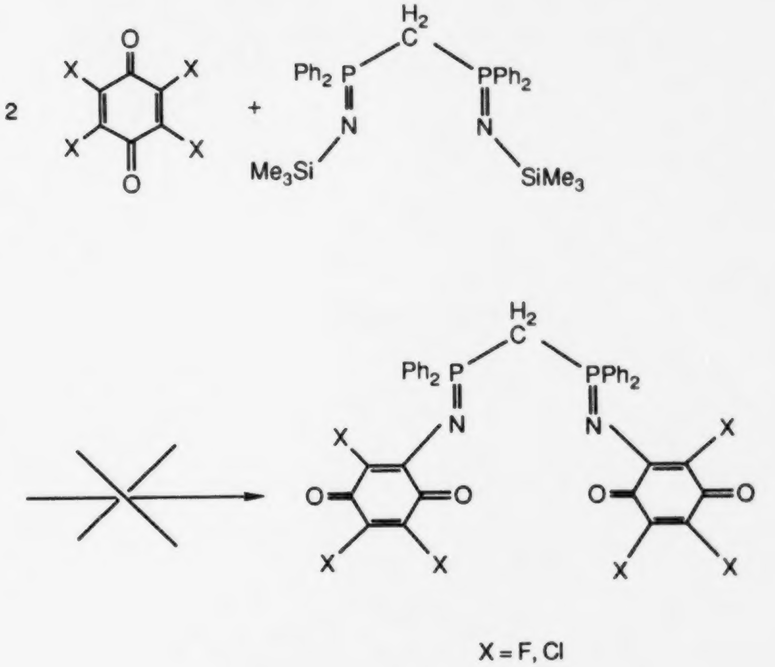
X=F, **3-6** : R$_3$ =Ph$_3$
3-7 : R$_3$ =Ph$_2$Me
3-8 : R$_3$ =PhMe$_2$
3-9 : R$_3$ =Ph$_2$CH$_2$PPh$_2$
X=Cl, **3-10** : R$_3$ =Ph$_3$
3-11 : R$_3$ =Ph$_2$Me

X=F, **3-1** : R$_3$ =Ph$_3$
3-2 : R$_3$ =Ph$_2$Me
X=Cl, **3-3** : R$_3$ =Ph$_3$
3-4 : R$_3$ =Ph$_2$Me
3-5 : R$_3$ =PhMe$_2$

X=F, **3-12** : R$_3$ =Ph$_3$ R'$_3$ =Ph$_2$Me
3-13 : R$_3$ =Ph$_3$ R'$_3$ =PhMe$_2$
3-14 : R$_3$ =Ph$_2$Me R'$_3$ =PhMe$_2$
3-15 : R$_3$ =Ph$_3$
R'$_3$ = Ph$_2$CH$_2$PPh$_2$
X=Cl, **3-16** : R$_3$ =Ph$_3$ R'$_3$ =Ph$_2$Me

Attempts to prepare bridged monosubstituted *p*-benzoquinone derivatives (Equation 3-1) by reaction of Me_3Si-N=P(Ph)$_2$PCH$_2$P(Ph)$_2$=N-SiMe$_3$ with two equivalents of halogenated *p*-benzoquinone were not successful. Initially a deep blue colored solution was observed, which changed gradually to a purple-red color, but the isolated products showed a complicated spectrum in the ^{31}P NMR and ^{19}F NMR spectra.

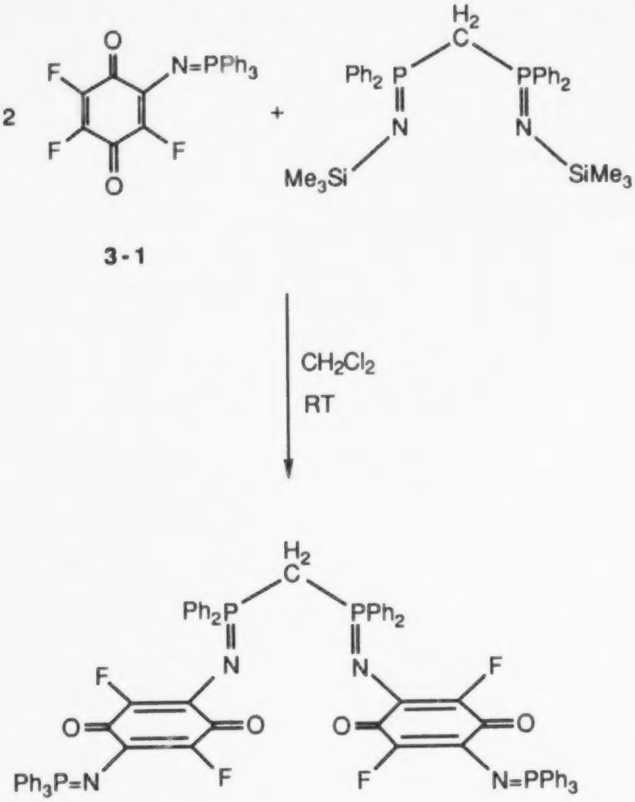
Equation 3-1:



However, the reaction of $Me_3Si\text{-}N{=}P(Ph)_2PCH_2P(Ph)_2{=}N\text{-}SiMe_3$ with the monosubstituted quinone derivative (**3-1**), yielded the stable product (**3-17**) (Equation 3-2).

Compound (**3-17**), like the other disubstituted quinone derivatives described herein, is air-stable and is soluble in most common organic solvents. The compound is green ($\lambda_{max} = 396$) and has a very high molar extinction coefficient ($\log \varepsilon = 4.70$). The constitution of the compound was determined from the elemental analyses, mass spectrum and ^1H, ^{31}P and ^{19}F NMR spectra. The molecular ion was observed in the mass spectrum. The ^{31}P NMR spectrum shows two singlets at 6.47 and 14.66 ppm, which shows that there exist only two environments for ^{31}P, and so the structure must be symmetrical. Since most ^{31}P chemical shifts for $Ph_3P{=}N\text{-}$ groups in benzoquinone derivatives are at about 14-15 ppm, it is reasonable to assign the peak at 14.66 ppm in (**3-17**) to the $Ph_3P{=}N$- group, and the peak at 6.47 ppm to the $-N{=}PPh_2\text{-}CH_2$- group.

Equation 3-2:



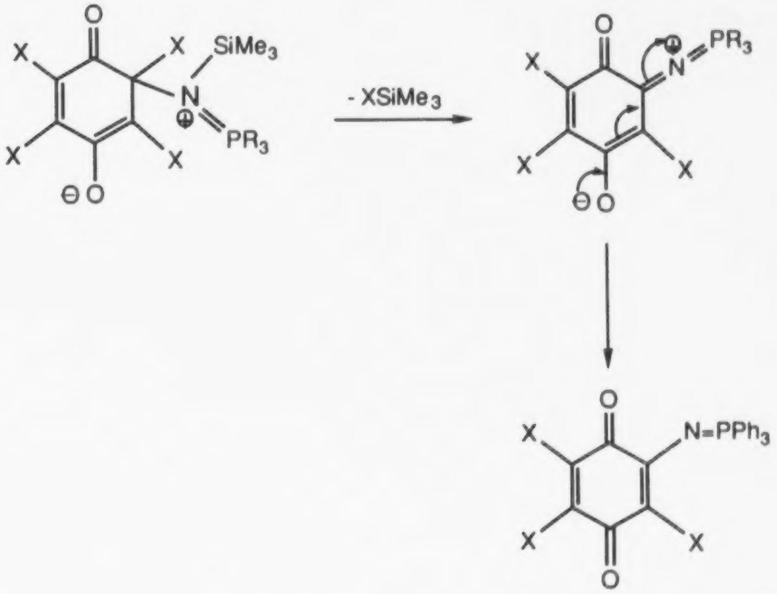
3-1

3-17

3.1.2. Proposed Mechanism for the Substitution of Halogenated *p*-Benzoquinone with $R_3P{=}NSiMe_3$

The rate of substitution for halogenated *p*-benzoquinones is F > CN > Cl, which corresponds to the order of electronegativity. Thus, the observed order in rates is consistent with a vinyl substitution mechanism: addition-elimination mechanism (Scheme 3-2).[165]

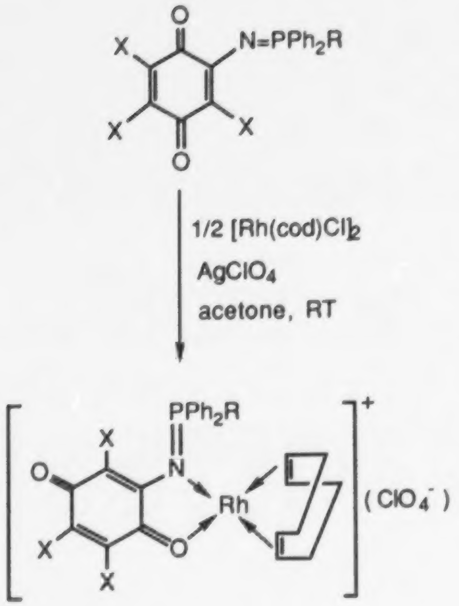
Scheme 3-2:



3.1.3. Complexation Reaction of Monosubstituted *p*-Benzoquinone with $[Rh(cod)Cl]_2$ and $AgClO_4$

Reactions of (**3-1**) or (**3-4**) with $1/2[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C gave the corresponding complexes (**3-18**) and (**3-19**) in high yield (Equation 3-3).

Equation 3-3:



3-18 : X = F, R = Ph
3-19 : X = Cl, R = Me

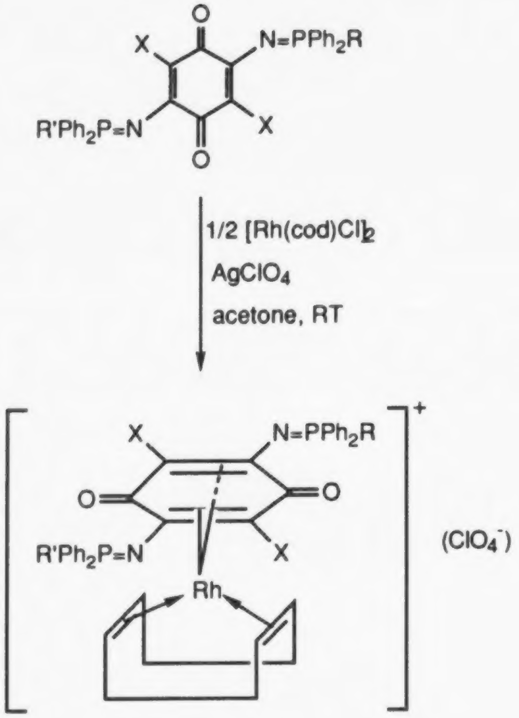
A parent peak with the mass of monometallic cationic unit for each of the complexes above is observed in the mass spectra (FAB). The ^{31}P NMR chemical shift of complex **3-18** shows a single peak at 39.2 ppm, which is 23.9 ppm downfield from the signal for the corresponding uncoordinated ligand **3-1**. The ^{19}F NMR of complex **3-18** showed three signals at -140.43 ppm (dd, 1.5 and 4.9 Hz), -148.33 ppm (d, 4.9 Hz, *para* to the phosphinimine) and -158.76 ppm (s, *ortho* to the phosphinimine), whereas in the uncoordinated ligand **3-1** the ^{19}F NMR chemical shifts showed corresponding signals at -141.92 ppm (d, 7.5 Hz), -148.36 ppm (dd, 3.8 and 7.5 Hz, *para* to the phosphinimine) and -152.55 ppm (d, 3.8 Hz, *ortho* to the phosphinimine). Comparing the ^{19}F NMR chemical shifts between the complex and the ligand, the signal at -140.43 ppm showed only a 1.5 ppm downfield shift compared with that of the ligand, and there is no significant shift for the signal at -148.3 ppm. However, the third signal (-158.76 ppm), which characterizes the fluorine closest to the phosphinimine, showed a 6 ppm upfield shift compared with that of the uncoordinated ligand. These data are consistent with a structure in which the imine nitrogen is coordinated to the Rh center. There is no evidence for Rh-F coupling, which is about 10 Hz for compounds of the structures (**3-20**) - (**3-22**) below. The infra-red spectrum of the complex (**3-18**) showed two C=O stretching bands at 1692 and 1664 cm^{-1} compared with the bands at 1709 and 1685 cm^{-1} for the corresponding uncoordinated ligand (**3-1**). The change in value is probably caused by π back donation from the Rh center to the C=O π^* orbital. Therefore, based on the above evidence, it is proposed that complex (**3-18**) contains rhodium coordinated by the ligand *via* both an oxygen and an imine nitrogen, as illustrated in Equation 3-3.

The ^{31}P NMR spectrum for complex **3-19** showed a single peak at 31.2 ppm, which is 16 ppm downfield from the corresponding uncoordinated ligand **3-4**. The C=O infra-red stretching frequencies of complex **3-19** are at 1681 and 1629 cm^{-1}, compared with the corresponding bands at 1725 and 1679 cm^{-1} for the uncoordinated ligand **3-4**. Therefore, complex **3-19** has a structure similar to that of complex **3-18**.

3.1.4. Complexation Reaction (π-Bonding Mode) of Disubstituted *p*-Benzoquinone with $[Rh(cod)Cl]_2$ and $AgClO_4$

The disubstituted ligands (**3-6**), (**3-7**), (**3-12**) and (**3-16**) reacted with $1/2[Rh(cod)Cl]_2$ and one equivalent of $AgClO_4$ to form cationic mononuclear complexes (**3-20**) - (**3-23**) (Equation 3-4).

Equation 3-4:


X
N=PPh$_2$R
R'Ph$_2$P=N
X
O
O
1/2 [Rh(cod)Cl]$_2$
AgClO$_4$
acetone, RT
X
N=PPh$_2$R
O
O
R'Ph$_2$P=N
X
Rh
+
(ClO$_4^-$)

3-20: X = F, R = Ph, R' = Ph
3-21: X = F, R = Me, R' = Me
3-22: X = F, R = Ph, R' = Me
3-23: X = Cl, R = Ph, R' = Me

A parent peak for the monometallic cationic unit for each of the complexes was observed in the mass spectra (FAB), and the elemental analyses are consistent with these formulae. The ^{31}P NMR spectra showed a singlet at 24.84 and 28.19 ppm for (**3-20**) and (**3-21**) respectively, and two single peaks at 24.99 and 28.14 ppm for (**3-22**) and at 24.30 and 27.19 ppm for (**3-23**) respectively. The ^{19}F NMR spectra showed a doublet at -178.1 ppm for (**3-20**) and a doublet at -178.3 ppm for (**3-21**), respectively. The coupling constant is 10.2 Hz for each case and it can be attributed to coupling between Rh and F (Figure 3-1).

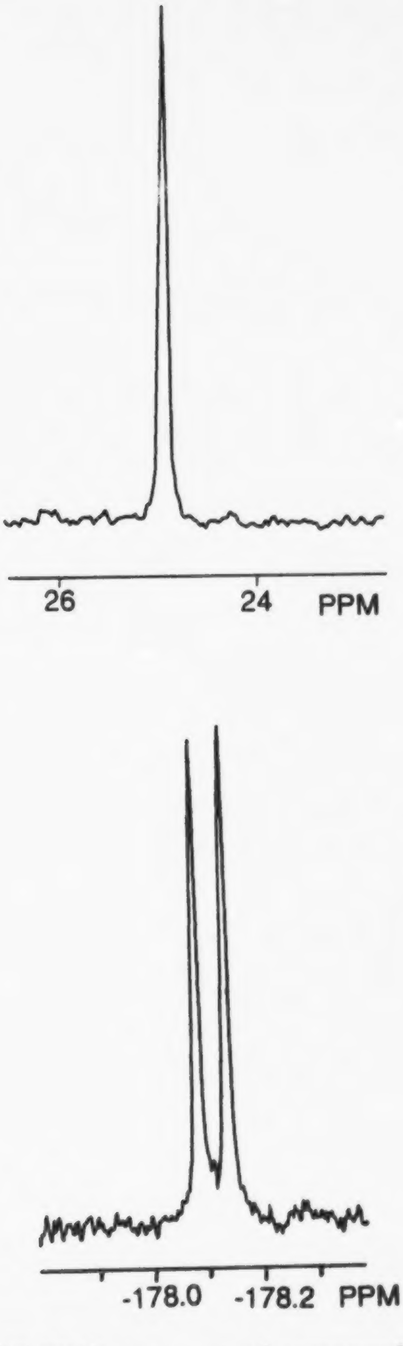


Figure 3-1 (Top) ^{31}P NMR spectrum of compound (**3-20**); (Bottom) ^{19}F NMR spectrum of compound (**3-20**).

For **(3-22)** the ^{19}F NMR data showed a complicated spectrum comprising two main groups of signals centered at -178.4 and -179.1 ppm. Each group contains multiple signals from various couplings. The $^{19}F\{^1H\}$ decoupled spectrum is a doublet of doublets of doublets for each group signal with coupling constants of 1.7, 3.1 and 10.2 Hz. The $^{19}F\{^{31}P\}$ decoupled spectrum is simplified to a doublet of doublets for each group of signals, with fine structure arising from very small couplings to ^1H. The two principal coupling constants are 3.0 and 10.2 Hz respectively, and the $^{19}F\{^1H, ^{19}F$ at -179.1 ppm$\}$, the decoupled spectrum of ^1H and homonuclear ^{19}F decoupling at -179.1 ppm, gives a signal at -178.4 ppm comprising a doublet of doublets with coupling constants of 1.3 and 10.0 Hz. Thus the coupling constants are assigned as follows: $^2J_{Rh\text{-}F} = 10.2$ Hz, $^5J_{F\text{-}F} = 3.0$ Hz and $^4J_{P\text{-}F} = 1.3$ Hz; $J_{H\text{-}F}$ is less than 0.5 Hz. The value of $^2J_{Rh\text{-}F} = 10.2$ Hz is the same as the corresponding parameter for **(3-21)**. The small coupling $^4J_{P\text{-}F} = 1.3$ Hz observed from $^{19}F\{^1H, ^{19}F$ at -179.1 ppm$\}$ decoupled spectrum was not observed in the ^{31}P NMR spectrum. For complex **(3-23)**, in which there are no fluorine substituents in the quinone ring, both ^{31}P signals show values for chemical shifts close to those of **(3-22)**. Thus, it is suggested that complex **(3-23)** also possesses a π-complex structure.

The UV spectra of each of the above complexes show bathochromic shifts upon complexation. The complexes are brown, whereas the corresponding ligands are green. The λ_{max} for the complexes **(3-20)**, **(3-21)** , **(3-22)** and **(3-23)** are 400 nm (25000 cm^{-1}), 400 nm, 448 nm and 400 nm respectively, whereas for the corresponding ligands **(3-6)**, **(3-7)**, **(3-12)** and **(3-16)** the λ_{max} are 386 nm, 386 nm, 385 nm and 388 nm respectively. The complexes show reduced absorption intensity (log ε values are 4.47, 4.16 , 4.09 and 4.04 respectively) relative to that of the free ligands (log ε values are 4.58, 4.48, 4.27 and 4.25 respectively). In addition to these absorption maxima, a less intense absorbance occurs at 574 nm, 564 nm, 565 nm and 566 nm, respectively in the UV spectra for each of the complexes.

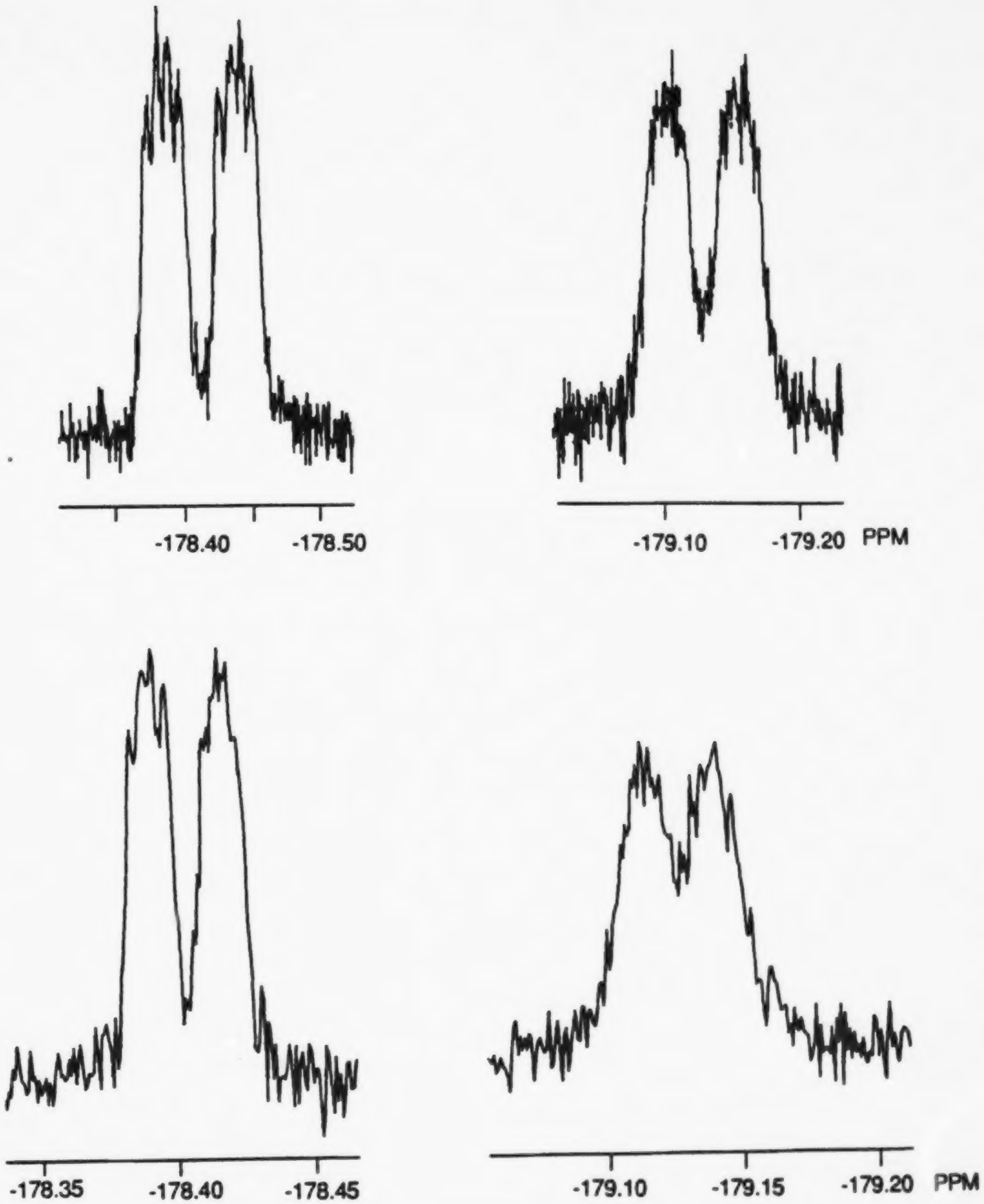


Figure 3-2 (Top): ^{19}F NMR spectrum of complex (**3-22**); (Bottom): ^{19}F{^{1}H} NMR spectrum of complex (**3-22**).

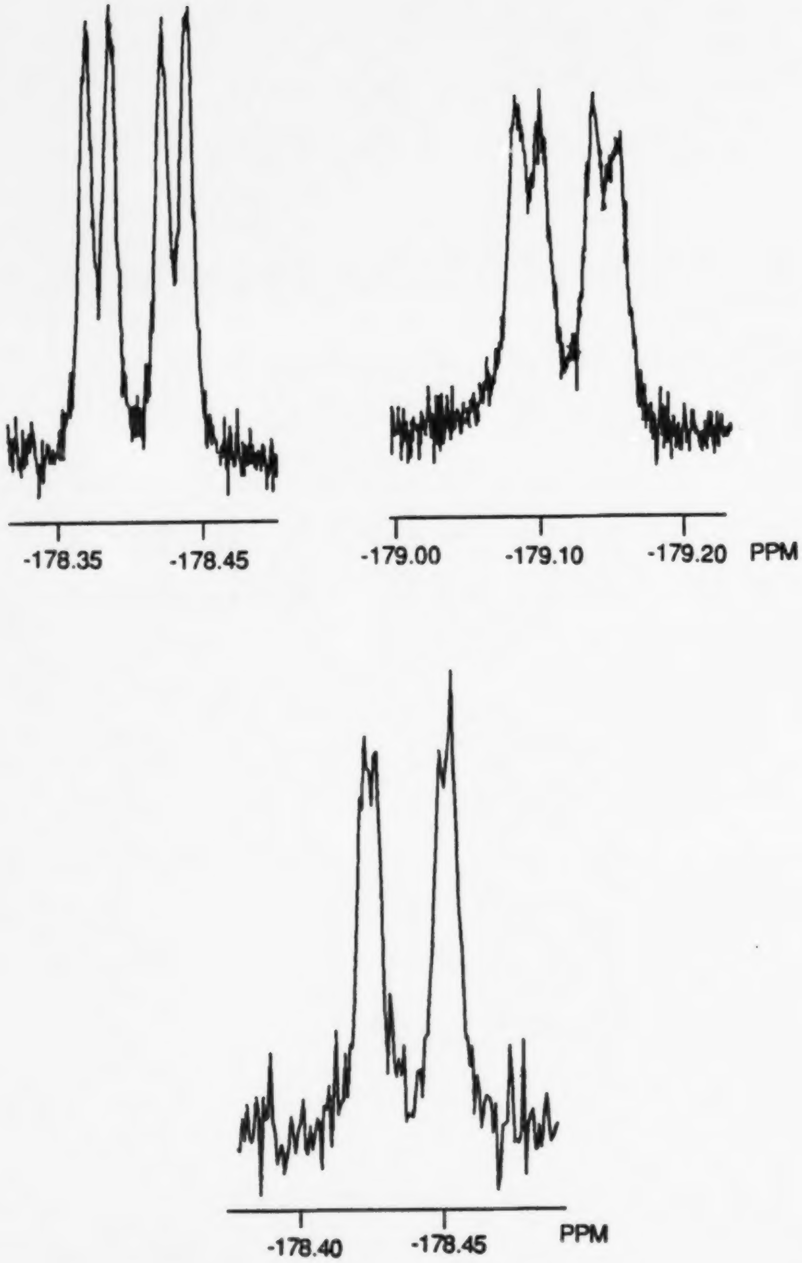
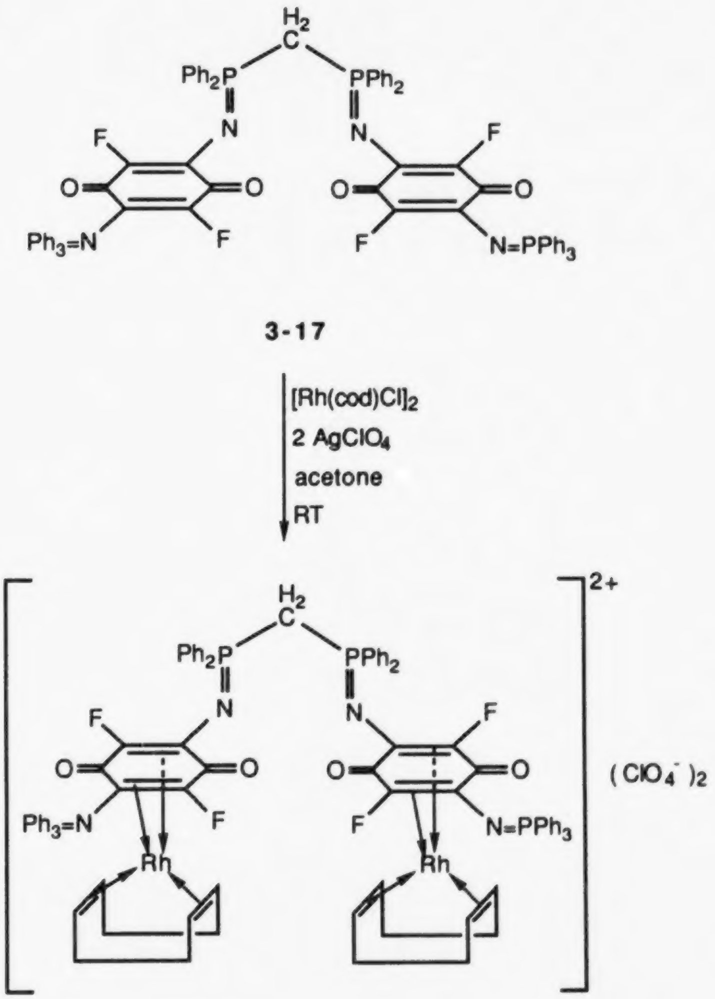


Figure 3-3 (Top): $^{19}F\{^{31}P\}$ NMR spectrum of complex (**3-22**); (Bottom): $^{19}F\{^{1}H$, ^{19}F at -179.1 ppm$\}$ NMR spectrum of (**3-22**).

The reaction of ligand (**3-17**) with one equivalent of $[Rh(cod)Cl]_2$ and two equivalents of $AgClO_4$ gave a dinuclear dicationic complex (**3-24**) (Equation 3-5). The reaction of the ligand with the starting Rh precursor in solution is fast, and a rapid color change from the characteristic green color of the ligand to the brown color of the complex is observed immediately upon mixing.

Equation 3-5:



3-17

3-24

The elemental analyses are consistent with the proposed formula. The monocation $[LRh(cod)]^+$ signal was observed in the mass spectrum (FAB). $[LRh_2(cod)_2]^+$ was not observed because it is beyond the observable mass range. The molecular weight in CH_2Br_2 solution was determined using a Corona Wescan Vapor Pressure Osmometer. The result obtained (1655) is close to the calculated molecular weight (1870) of (**3-24**). The ^{31}P NMR spectrum of the complex showed two single peaks at 18.85 and 24.78 ppm respectively, each of which are shifted significantly downfield compared with the values for the uncoordinated ligand. The chemical shift at 24.78 ppm is assigned to the PPh_3 group because it is very close to that for complex (**3-20**), in which the corresponding unit gives a chemical shift of 24.84 ppm. The ^{19}F NMR spectrum is very similar to that of (**3-22**), and the coupling constant values for (**3-24**) are: $^2J_{Rh\text{-}F} = 10.5$ Hz, $^5J_{F\text{-}F} = 3.0$ Hz, $^4J_{P\text{-}F} = 1.3$ Hz.

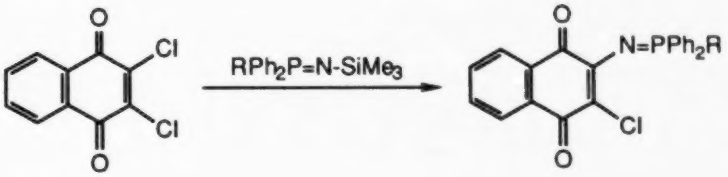
The reactions of the disubstituted ligands (**3-6**), (**3-7**) and (**3-12**) with $[Rh(cod)Cl]_2$ and two equivalents of $AgClO_4$ were carried out in attempts to prepare the σ-coordinated dinuclear complexes. However, the ^{31}P NMR and ^{19}F NMR chemical shifts are exactly the same as those for (**3-20**), (**3-21**) and (**3-22**). Therefore, it is proposed that these products are not the target σ-coordinated dinuclear complexes but are instead the π-coordinated mononuclear complexes, (**3-20**), (**3-21**) and (**3-22**) respectively.

The similar reaction of the potentially tetradentate ligand (**3-17**) with two equivalents of $[Rh(cod)Cl]_2$ and four equivalents of $AgClO_4$ was carried out in an attempt to form the σ-coordinated tetranuclear complex. However, the observed ^{31}P NMR and ^{19}F NMR chemical shifts are the same as that of (**3-24**). Again, it is proposed that the expected σ-coordinated tetranuclear complex is not formed and the actual product is the π-coordinated dinuclear complex (**3-24**).

3.1.5. Synthesis of Mono-phosphinimine Substituted *p*-Naphthoquinone Derivatives

Similar to tetrafluoro- or tetrachloro-*p*-benzoquinone, the reaction of 2,3-dichloro-*p*-naphthoquinone with one equivalent of a series of trimethyl phosphinimines in CH_2Cl_2 gave a series of mono-substituted *p*-naphthoquinone derivatives (**3-25**) and (**3-26**) in high yields (Equation 3-6). No further substituted derivatives were observed.

Equation 3-6:



3-25: R = Ph
3-26: R = Me

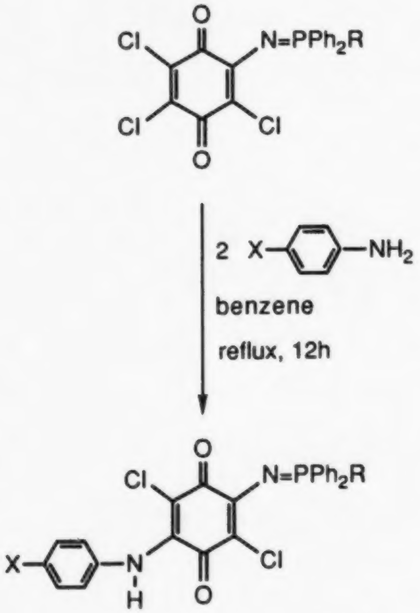
Molecular ions for each of the compounds have been observed in the mass spectra. Phosphorus-31 NMR data are given in Table 3-1. The ^{31}P NMR spectra for (**3-25**) and (**3-26**) show a singlet at 13.4 ppm and 14.2 ppm, respectively, which are about 1 ppm upfield compared with analogs chlorobenzoquinone derivatives (**3-3**) and (**3-4**). Compounds (**3-25**) and (**3-26**) are each air-stable solids and are soluble in most common organic solvents. Each one is red and has a high UV-visible molar extinction coefficient.

3.2. Phosphinimine and Aniline Mixed Disubstituted Chloro-*p*-Benzoquinone Derivatives and Their Cationic Rh(I) Complexes

3.2.1. Synthesis and Properties of the Ligands

The reaction of 3,5,6-trichloro-2-(phosphinimino)-*p*-benzoquinone with two equivalents of *p*-X-$C_6H_4NH_2$ gave a series of disubstituted *p*-benzoquinone derivatives (**4-1**) - (**4-8**) in good yields (Equation 3-7).

Equation 3-7:


Cl
O
N=PPh2R
Cl
Cl
O
2 X–⬡–NH2
benzene
reflux, 12h
O
Cl
N=PPh2R
X
N
H
Cl
O

R = Ph, X = F, Cl, Me, NH_2

4-1, 4-2, 4-3, 4-4

R = Me, X = F, Cl, Me, NH_2

4-5, 4-6, 4-7, 4-8

Each of the above disubstituted compounds is an air-stable, green colored solid which is soluble in most organic solvents. Each one has a high molar extinction coefficient in solution (Table 3-2). The composition and structure of each of the compounds has been determined from the analytical data, mass spectra and ^1H and ^{31}P NMR spectroscopy. Molecular ions for each of the compound have been observed in the mass spectra. Phosphorus-31 NMR data are given in Table 3-2. The ^{31}P chemical shifts of each of the disubstituted compounds show a downfield shift of approximately 1.5 ppm compared with those of the monosubstituted precursors. The ^1H NMR spectra for each complex show a single peak close to 8.3 ppm, which is assigned to the N-H component of the phenylamine substituent. The IR spectra for each compound show a strong band around 3250 cm^{-1} which is the N-H stretching frequency.

The X-ray crystal and molecular structure has been determined[141] for **(4-3)** as a representative example of these new compounds. The ORTEP[142] plot for **(4-3)** is shown in Figure 3-4.

Selected bonding parameters and the X-ray crystallographic data are given in Tables (4-2)-(4-5). The P-N bond length (1.612(6) Å) for **(4-3)** is longer than those shown by phosphinimine groups bound to fluoroaromatics (1.567-1.589 Å) (Chapter 2) as previously reported,[5] but the distance lies within the range of values for covalent radii (1.64Å)[145] for a P-N double bond.

The P-N(1)-C(3) angle is 130.7(5)°, which is much smaller than that in $Ph_3P{=}N{-}SiMe_3$ in which the P-N-Si is 150°.[166] In the structure of $Ph_3P{=}N{-}SiMe_3$, the N atom is in a sp^2 hybrid geometry, Ph_3P and $SiMe_3$ are both good π acids. The filled p orbital of the N atom is perpendicular to the sp^2 plane. The empty σ^* orbital of the P atom, the filled p orbital of the N atom and the empty σ^* orbital of the Si atom are in the same plane. This three center-two electron, π delocalized interaction stabilizes the sp^2 geometry at the N atom. Most importantly, these two groups are very bulky, but they have to be in the same molecular plane to satisfy the electronic requirement mentioned above, eg. the delocalization through the sp^2 hybridized center. Accomodating these two bulky groups in the same plane, requires that the bond angle has to be opened further than 120°.

In the structure of **(4-3)**, and in the structures of **(1-1)**, **(1-2)**, and **(2-1)** - **(2-3)**, the angles of R_3P=N-C(phenyl of quinone ring) are about 129 - 140°. This is caused by significant steric repulsion between the β position (F atom in phenyl ring, or O atom in quinone ring) and the R group due to the co-planar property of the sp^2 nitrogen center. Therefore, the R_3P=N-C angles are larger than 120°, but smaller than 150°, because the repulsion in R_3P=N-C systems is smaller than that in the R_3P=N-$SiMe_3$ case.

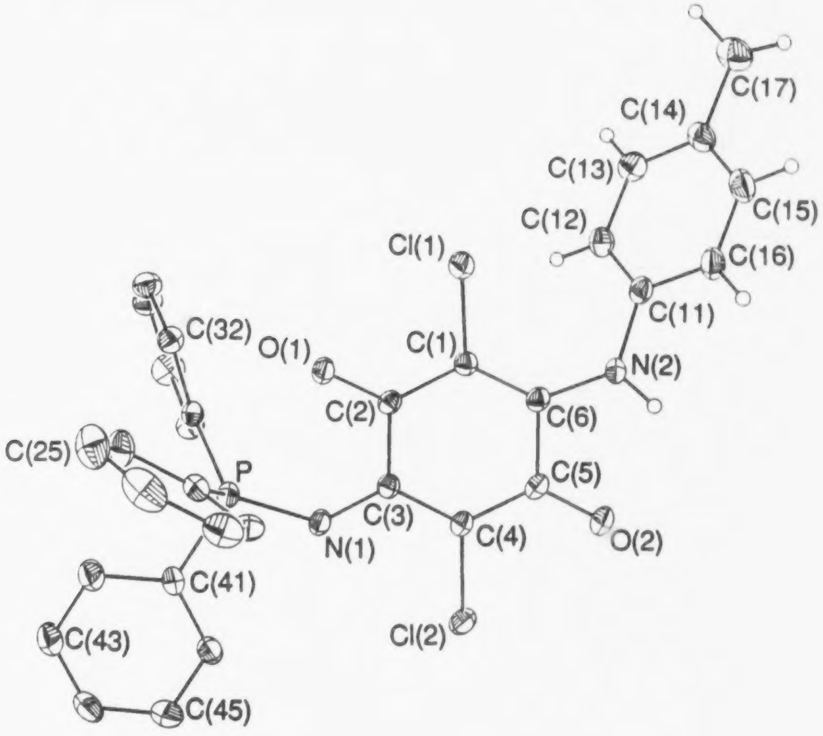
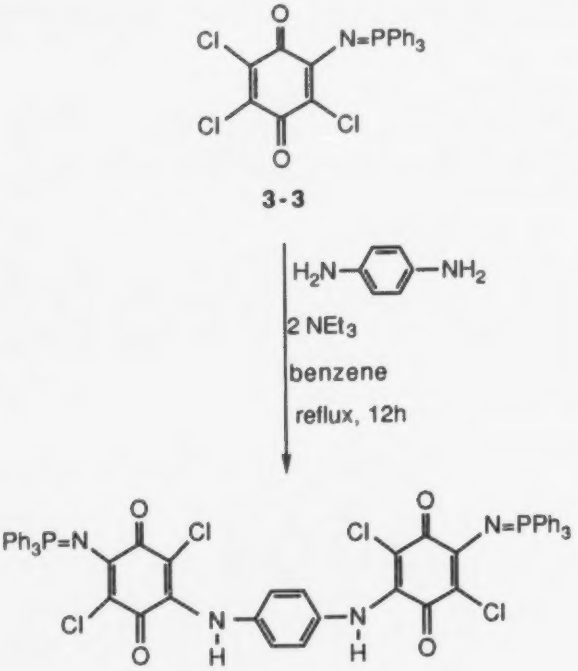

C(17)
C(14)
C(13)
C(15)
C(12)
C(16)
Cl(1)
C(11)
C(32)
O(1)
C(1)
N(2)
C(2)
C(6)
C(25)
P
C(5)
C(3)
N(1)
C(4)
O(2)
C(41)
C(43)
Cl(2)
C(45)

Figure 3-4. ORTEP Perspective view of (**4-3**) showing the atom numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms on the phenylamine substituent are shown but those on the phenyl substituents of the Ph_3P unit are not.

Reaction of two equivalents of 3,5,6-trichloro-2-(phosphinimino)-*p*-benzoquinone with one equivalent of 1,4-phenyldiamine and two equivalents of triethylamine gave (**4-9**) (Equation 3-8).

Equation 3-8:

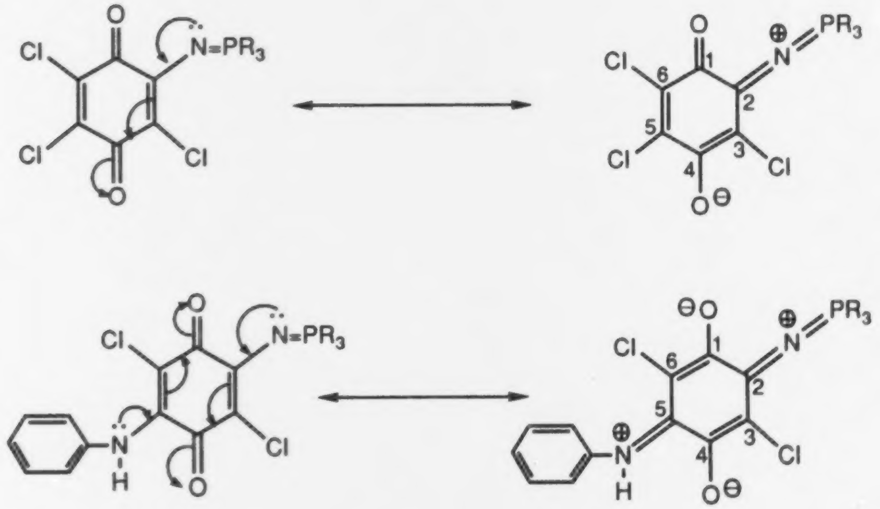

O
Cl
N=PPh$_3$
Cl
Cl
O
3-3
H$_2$N
NH$_2$
2 NEt$_3$
benzene
reflux, 12h
Ph$_3$P=N
O
Cl
Cl
O
N=PPh$_3$
Cl
N
H
N
H
Cl
O
O

4-9

Use of the stoichiometric amount of triethylamine gives a clean reaction. Like compounds (**4-1**) - (**4-8**), compound (**4-9**) is an air-stable, green solid which is soluble in most organic polar solvents. It also shows a high molar extinction coefficient. The molecular ion was observed in the mass spectrum. The ^{31}P NMR chemical shift shows a single peak at 15.81 ppm, which is about 1.4 ppm downfield compared with that for the precursor (**3-3**). The presence of only one environment for ^{31}P means that the two phosphimine groups are chemically equivalent. ^{1}H NMR shows a single peak at 8.32 ppm which is again assigned to the N-H component. The N-H stretch is observed at 3264 cm^{-1} in the IR spectrum.

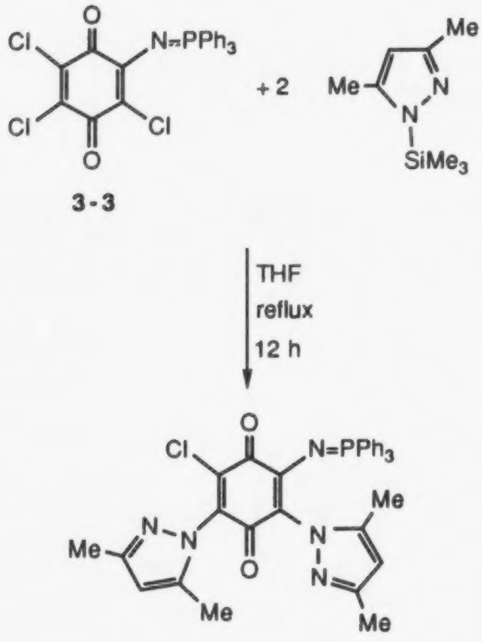
Each of the monosubstituted benzoquinone derivatives can react with another equivalent of either $R_3P=N-SiMe_3$ or aniline to form mixed disubstituted derivatives. In the latter case a second equivalent of aniline is required to complex the HCl. The second substitution always occurs at the C5 position of the monosubstituted quinone derivative. No further substitution occurs, presumably because, in *p*-benzoquinone, the power of the C=O to activate meta substituents is reduced when the lone pair of the imine nitrogen delocalizes and quenches the activating power of the C=O. Therefore the chlorine at C6 is deactivated, whereas the lone pair in the imine nitrogen does not affect the C=O in position 1 (Scheme 3-3). The C=O in position 1 activates the meta chlorines in C3 and C5, but the chlorine in C3 is sterically hindered so the second substitution occurs at C5. If this second substituent also has a lone pair, the same delocalization will deactivate the C=O in position 1. Therefore, both electronic and steric factors block further substitution at the remaining chlorines (C3 and C6).

Scheme 3-3:



When the connecting atom in the second substituted group has no lone pair, it is then expected that the C=O in position 1 will not be deactivated and will be able to further activate the chlorine in C3 toward substitution. This prediction has been confirmed by the following reaction (Equation 3-9).

Equation 3-9:



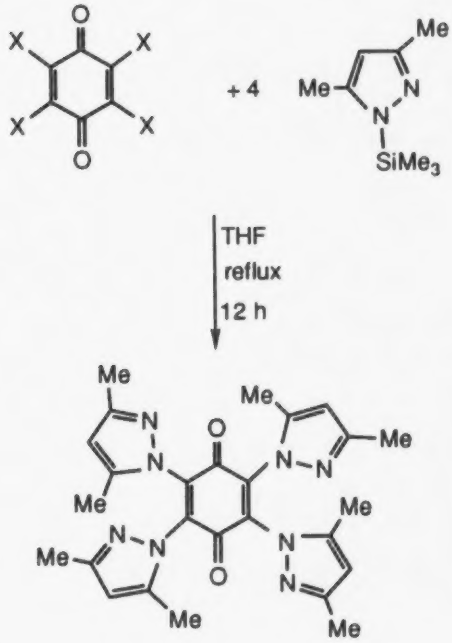
3-3

4-10

When the monosubstituted precursor (**3-3**) was treated with two equivalents of N-trimethylsilyl-3,5-dimethylpyrazole, chlorine atoms at both C3 and in C5 positions were easily substituted, but no further substitution occured. The molecular ion of the compound (**4-10**) was observed in the mass spectrum. ^{31}P NMR showed a single peak at 15.02 ppm, which is about 0.6 ppm downfield from that of (**3-3**). ^{1}H NMR spectrum clearly showed two distinct C-H signals, and four different methyl groups. The above reaction proceeds so quickly that it is not possible to carry it out in a stepwise manner. A reaction was performed with a 1:1 ratio of (**3-3**) with trimethylsilyl-3,5-dimethylpyrazole in an attempt to prepare the disubstituted quinone derivatives, but the main products were only (**4-10**) and some unreacted precursor (**3-3**). Only a small amount of disubstituted quinone derivative was obtained.

If there is no lone pair in the connecting atoms in the first and second substituted groups, all four chlorines can be substituted (Equation 3-10).

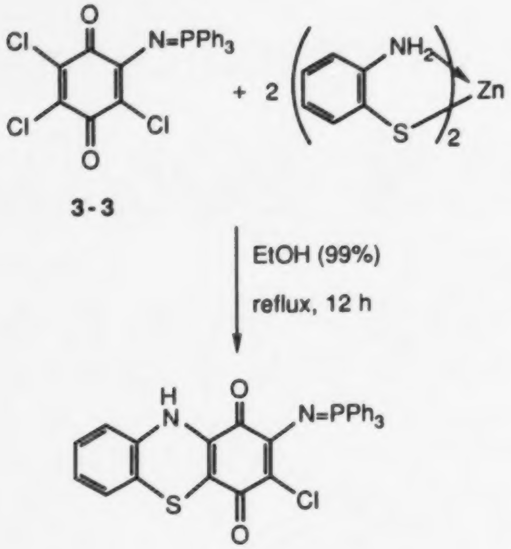
Equation 3-10:



Similar results were obtained starting from tetrafluoro-1,4-benzoquinone, tetrachloro-1,4-benzoquinone or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Each of these reactions also proceeds so quickly that it is not possible to restrict the extent of the reaction and obtain the mono or disubstituted derivatives.

Reaction of (**3-3**) with zinc 2-aminobenzenethiolate gave the product (**4-11**) (Equation 3-11).

Equation 3-11:



3-3

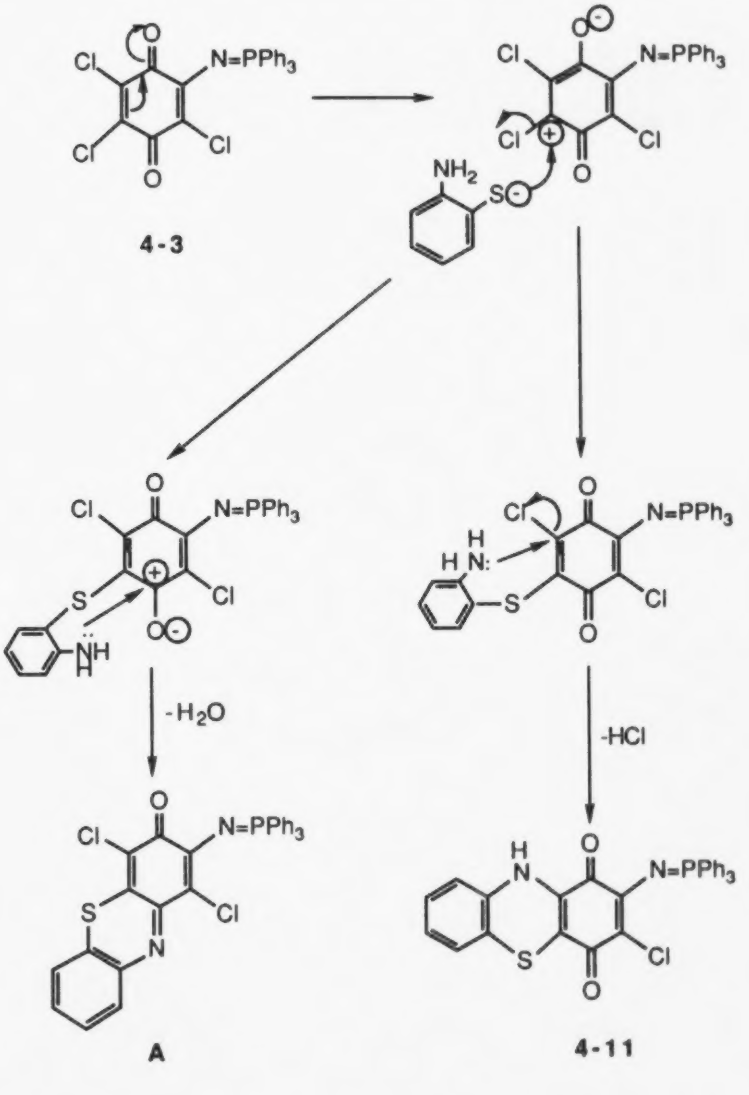
4-11

The molecular ion of compound (**4-11**) was observed in the mass spectrum. The phosphorus-31 NMR spectrum showed a single peak at 15.71 ppm, which is 1.3 ppm downfield from that of (**3-3**). The ^{1}H NMR spectrum showed a single peak at 8.25 ppm which corresponds to N-H, and the IR spectrum showed a strong peak at 3274 cm^{-1} which is the $\nu_{N\text{-}H}$ stretching frequency. Compound (**4-11**) is brown; the maximum absorption at 396 nm has a very high molar extinction coefficient (log $\varepsilon = 4.98$). Like the compounds (**4-1**) - (**4-10**), compound (**4-11**) has very good solubility in most organic polar solvents.

Zinc 2-aminobenzenethiolate was prepared from commercial 2-aminobenzenethiol by Mital's method.[167] It is necessary for smooth reaction to use zinc 2-aminobenzenethiolate rather than 2-aminobenzenethiol. Use of excess zinc 2-aminobenzenethiolate is also necessary (1 : 2 ratio) to increase the yield of product.

A possible mechanism is as follows (Scheme 3-4).

Scheme 3-4:

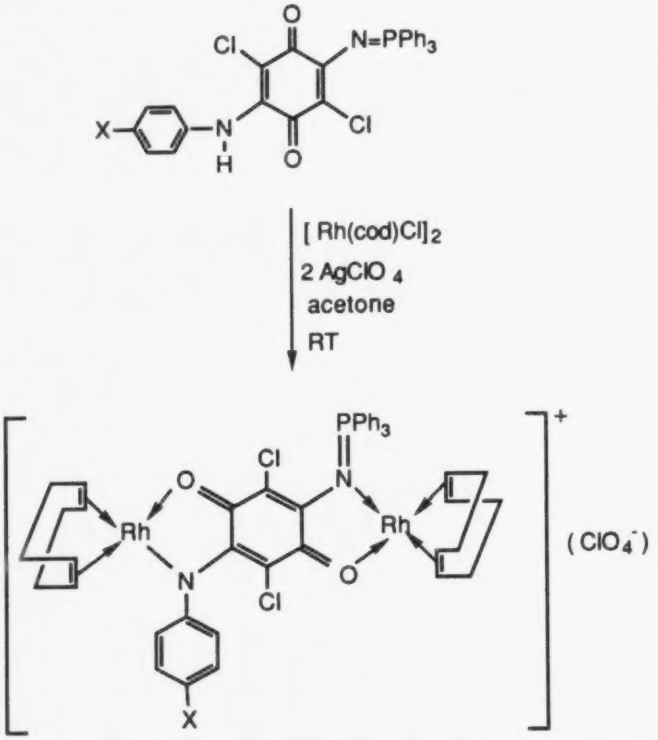


The mass of A was observed in the mass spectrum (EI) with small intensity.

3.2.2. Complexation Reactions of (4-1), (4-2) and (4-3) with $[Rh(cod)Cl]_2$/ $2AgClO_4$

The compounds (**4-1**), (**4-2**) and (**4-3**) reacted with one equivalent of $[Rh(cod)Cl]_2$ and two equivalents of $AgClO_4$ in acetone at 25 °C to give a series of dinuclear complexes, (**4-12**), (**4-13**) and (**4-14**) (Equation 3-12).

Equation 3-12:

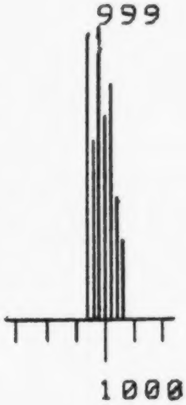

O
Cl
N=PPh3
X
N
H
Cl
O
[Rh(cod)Cl]2
2 AgClO 4
acetone
RT
PPh3
Cl
O
N
Rh
Rh
N
O
Cl
X
+
(ClO4-)

X = F, Cl, Me,

4-12, 4-13, 4-14,

A molecular ion for the dinuclear monocationic unit of the complex was observed in the mass spectra (FAB). Each of the the isotopic patterns is very close to those calculated. One representative example (mass spectrum of (**4-13**)) is shown in

Figure 3-5. The experimental spectrum (top) shows the highest peak at 999, and is consistent with the calculated spectrum (bottom).



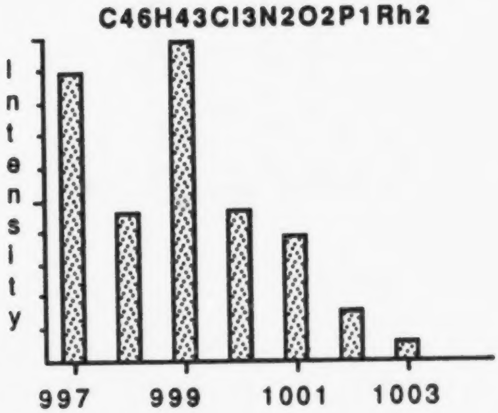


Figure 3-5. Mass spectrum (FAB) of (**4-13**). (Top): Experimental; (Bottom): Calculated mass spectrum.

The elemental analyses for **(4-12)** - **(4-14)** are consistent with the proposed formulae, which are also supported by the following spectroscopic evidence. The ^{31}P NMR chemical shift for each of the complexes showed downfield shifts of about 14 ppm when compared with those for the corresponding ligands **(4-1)** - **(4-3)**. The ^{1}H NMR spectra showed that the N-H signals for the ligands **(4-1)**, **(4-2)** and **(4-3)** appeared at about 8.3 ppm whereas, in the ^{1}H NMR spectra of the corresponding complexes, no N-H signal was observed, indicating that the Rh-N bond is a covalent bond instead of a coordinate link (Figure 3-6). This is further confirmed by the IR data. The N-H stretching frequencies for the ligands **(4-1)** - **(4-3)** appeared at 3235, 3220 and 3251 cm^{-1} respectively, whereas in the corresponding complexes, no N-H peak is observed (Figure 3-7). The CO stretching frequencies for the ligand **(4-1)** are 1648 and 1577 cm^{-1} whereas, for the corresponding complex **(4-12)**, the CO stretching frequencies are 1630 and 1577 cm^{-1}, with a decrease of only 18 cm^{-1} for the first band. The CO stretching frequencies for the ligand **(4-2)** are 1651 and 1598 cm^{-1} whereas, for the corresponding complex **(4-13)**, the CO stretching frequencies are 1639 and 1576 cm^{-1}, which decreased 12 cm^{-1} for the first band and 22 cm^{-1} for the second band. The CO stretching frequencies for the ligand **(4-3)** are 1648 and 1613 cm^{-1} whereas, in the corresponding complex **(4-14)**, the CO stretching frequencies are 1630 and 1574 cm^{-1}, which decreased 18 cm^{-1} for the first band and 39 cm^{-1} for the second band. Each of these indicates the existence of π back donation from the filled d-orbitals of the Rh center to the CO π^* orbitals.

The reaction between the ligands and "Rh(cod)" precursor occurs immediately on mixing the two solutions; the color of the solution changes from green to brown. The UV spectra of the complexes showed 57-73 nm bathochromic shifts, and the intensities for each of the complexes is smaller than that for the corresponding ligands.

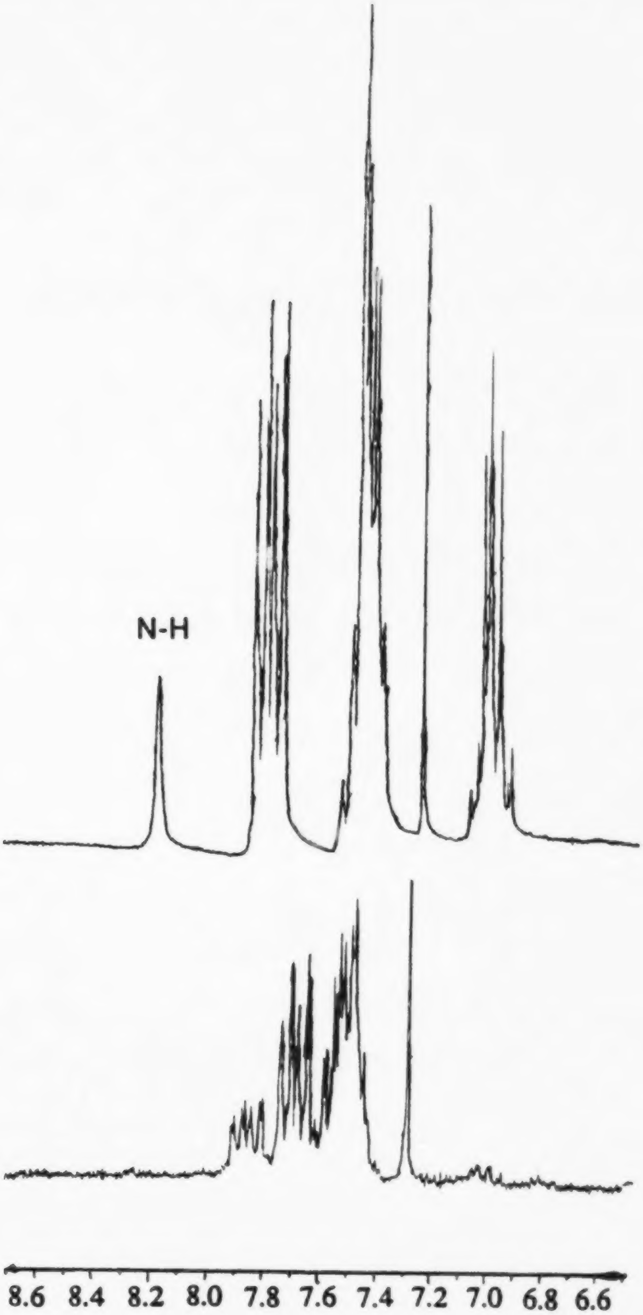
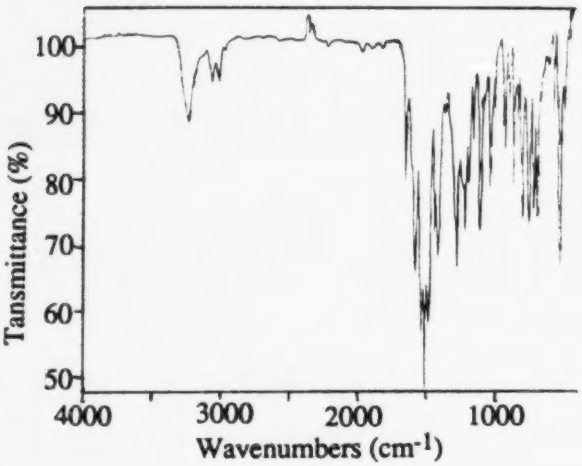


Figure 3-6. (Top): ^{1}H NMR of the ligand (**4-1**). (Bottom): ^{1}H NMR of the corresponding complex (**4-12**).



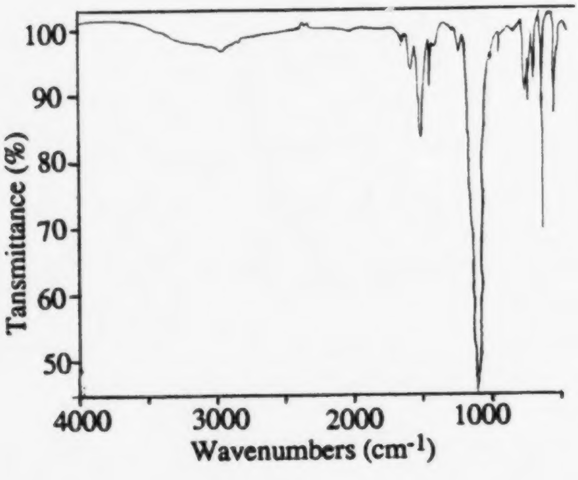
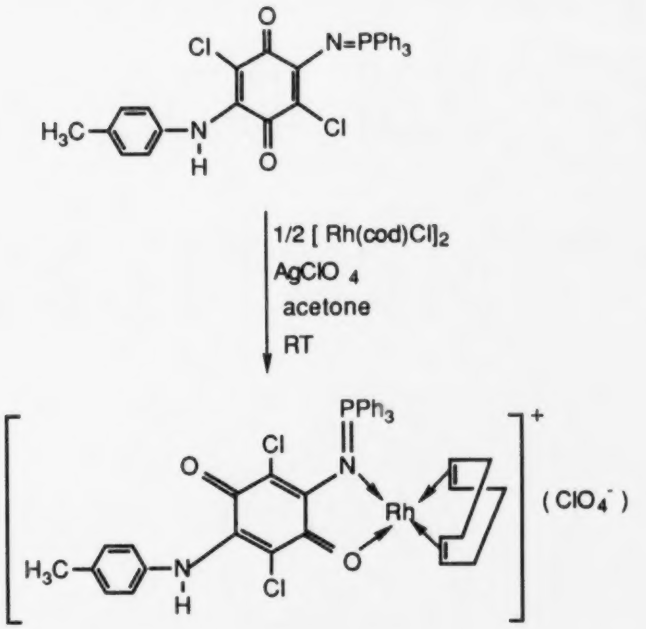


Figure 3-7. (Top): IR spectrum of the ligand (**4-2**). (Bottom): IR spectrum of the corresponding complex (**4-12**).

Compound (**4-3**) reacted with one-half equivalent of $[Rh(cod)Cl]_2$ and one equivalent of $AgClO_4$ in acetone at 25 °C to give a mononuclear complex, (**4-15**) (Equation 3-13).

Equation 3-13:



4-15

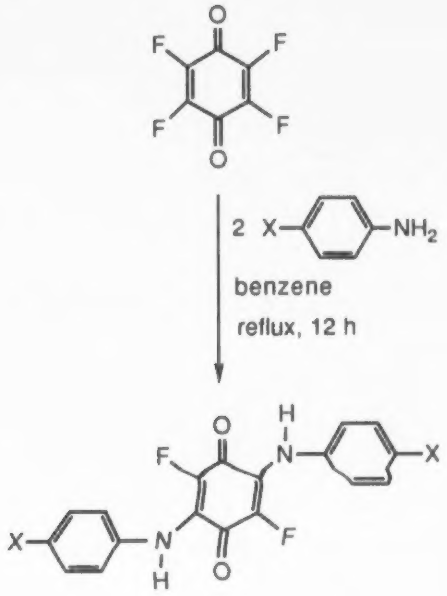
The highest mass peak observed in the (FAB) mass spectrum (732), corresponded to the ion [the monometallic cation - Cl]$^+$, derived from the cationic unit of the parent complex. The elemental analyses are consistent with the proposed formula. The ^{31}P NMR spectrum showed a single peak at 31.2 ppm which is 15.4 ppm downfield compared with the corresponding ligand (**4-3**) (15.8 ppm), and is only 1.2 ppm downfield from the corresponding signal for the dinuclear complex (**4-14**) (30.0 ppm). This chemical shift is also the same as that of the σ-coordinated mononuclear complex

(3-19) (31.2 ppm) suggesting that compound **(4-15)** is also a σ-coordinated complex. The ^{1}H NMR spectrum showed that a single peak at 8.0 ppm which is assigned to the N-H chemical shift, shifted upfield for 0.3 ppm compared with that of the corresponding ligand **(4-3)** (8.3 ppm). The IR spectrum shows a strong band at 3267 cm^{-1} which is assigned to the N-H stretching frequency, increased 16 cm^{-1} compared with that of the corresponding uncoordinated ligand **(4-3)** (3251 cm^{-1}).

3.2.3. Synthesis of 2,5-Bis-anilino-3,6-difluoro-*p*-benzoquinone Derivatives

Although 2,5-bis-anilino-3,6-dichloro, or dibromo-*p*-benzoquinone derivatives were reported a long time ago,[133] the fluorinated analogs have not been reported. The reaction of tetrafluoro-*p*-benzoquinone with two equivalents of *p*-X-$C_6H_4NH_2$ gave a series of disubstituted *p*-benzoquinone derivatives in very high yield (Equation 3-14).

Equation 3-14:



4-16: X= F
4-17: X= Cl
4-18: X= Br
4-19: X= I
4-20: X= CH_3
4-21: X= H
4-22: X= NO_2
4-23: X= NH_2

Here only two equivalents, instead of the four equivalents of aniline required for the chloride reactions, are needed to complete the reaction, because the eliminated HF forms HF_2^-.

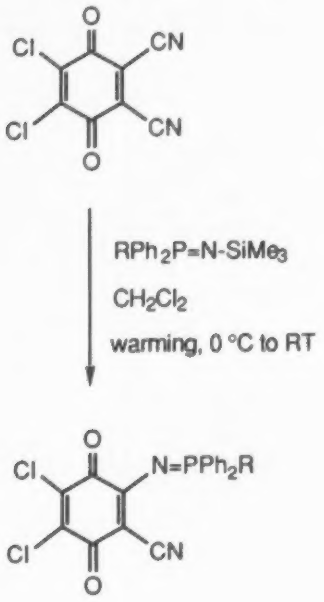
Molecular ions for each of the compounds above have been observed in the mass spectra. Each compound is deeply coloured and has a very high UV-visible molar extinction coefficient (Table 3-2). However, each compound has a very poor solubility and only dissolves in DMF or DMSO.

3.3 Phosphinimine Substituted Derivatives of 2,3-Dichloro-5,6-Dicyano-*p*-Benzoquinone, and Their Cationic Rh(I) Complexes

3.3.1. Synthesis and Properties of the Ligands

The reaction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone with one equivalent of trimethylsilyl phosphinimine in CH_2Cl_2 under mild conditions gave the monosubstituted derivatives (**5-1**) and (**5-2**) in good yields (Equation 3-15).

Equation 3-15:


O
Cl
CN
Cl
CN
O
RPh2P=N-SiMe3
CH2Cl2
warming, 0 °C to RT
O
Cl
N=PPh2R
Cl
CN
O

5-1: R = Ph
5-2: R = Me

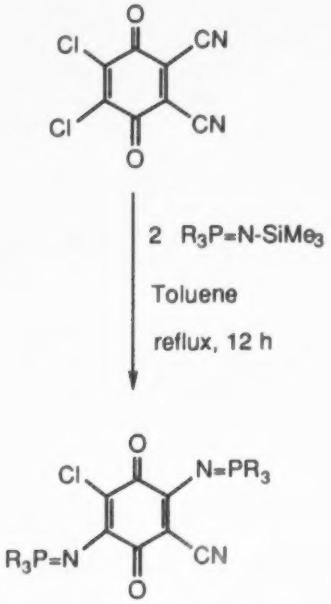
In this reaction, Me_3SiCN is eliminated instead of Me_3SiCl. The addition-elimination mechanism proposed for Equation 3-13 has been discussed earlier in this Chapter.

Since the electronegativity of CN is slightly greater than that of Cl, the carbon attached to the CN group in quinone is more positive than the carbon attached to Cl. Consequently, the imine nitrogen will preferentially attack the carbon attached to the CN group.

Compounds (**5-1**) and (**5-2**) are air-stable, purple solids which are soluble in most organic solvents. Both have high molar extinction coefficients (Table 3-7). The nature of each product has been deduced from elemental analyses, mass spectra, and ^{1}H and ^{31}P NMR spectroscopy. Molecular ions were observed in the mass spectra. Phosphorus-31 NMR data are given in Table 3-7. The ^{31}P signals for (**5-1**) and (**5-2**) appear at 18.45 ppm and 19.66 ppm respectively, which are about 4 ppm downfield from the shifts of the similar compounds 3,5,6-trichloro-2-(triphenylphosphinimino)-1,4-benzoquinone, (14.44 ppm) and 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-1,4-benzoquinone, (15.42 ppm) respectively (earlier of this Chapter).

Two equivalents of trimethylsilyl phosphinimine reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in refluxing toluene to form the disubstituted derivative. (Equation 3-16)

Equation 3-16:



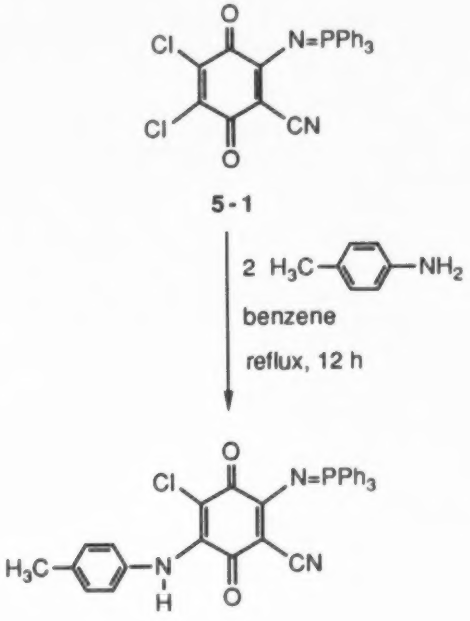
5-3: R = Ph

The molecular ion of (**5-3**) is observed in the mass spectrum. The ^{31}P NMR spectrum showed two singlets at 16.20 and 18.11 ppm respectively. Comparing these data with the chemical shifts of (**5-1**), it is reasonable to assign the peak at 18.11 ppm to the phosphinimine which is closest to the CN group, and the peak of 16.20 ppm to the phosphinimine which is closest to the Cl group.

Each of these substitutions (Equations 3-15 and 3-16) reflects the fact that, for the first substitution, the CN group is much more reactive to substitution on the quinone framework than the Cl group. The former can be eliminated at a very low temperature (-78 °C) whereas the latter requires much higher temperatures. For the second substitution, the C=O which is closest to the phosphinimine electronically activates the two meta positions, the second CN group and the chlorine *trans* to the phosphinimine, but the second CN group is sterically hindered by the phosphinimine. Therefore, the second substitution occurs at the chlorine *trans* to the phosphinimine.

The monosubstituted derivative (**5-1**) reacts with two equivalents of 4-methylaniline to form the disubstituted derivative (**5-4**) (Equation 3-17).

Equation 3-17:



5-1

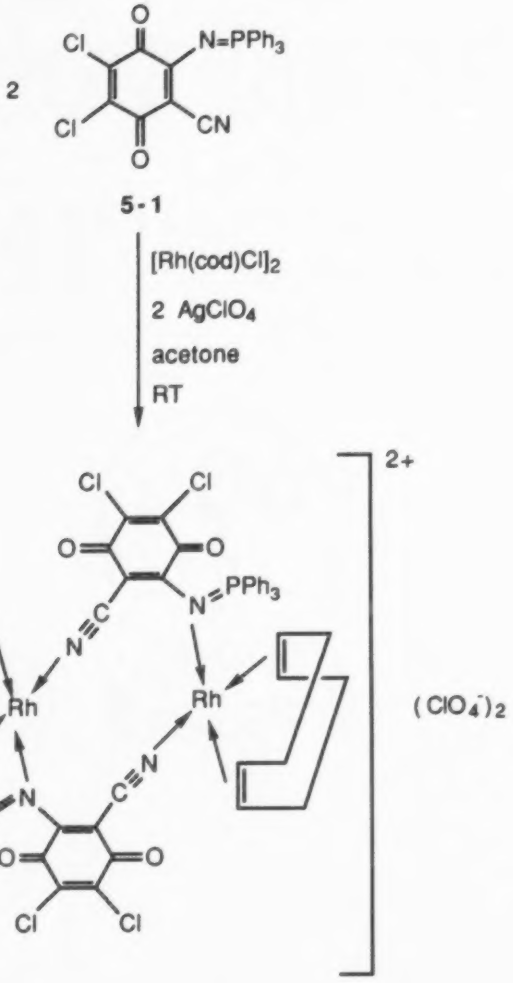
5-4

Compound (**5-4**) is an air-stable, dark brown solid which is soluble in most organic solvents. It has a high molar extinction coefficient (λ_{max} = 376 nm, log ε = 4.12). The molecular ion was observed in the mass spectrum. The ^{31}P NMR spectrum showed a single peak at 19.43 ppm, which is about 1 ppm downfield compared with that for the monosubstituted precursor. The ^{1}H NMR spectrum showed a singlet at 8.40 ppm which is assigned to the N-H group of the phenylamine substituent. The IR spectrum showed a strong peak around 3250 cm^{-1} which is the N-H stretching frequency.

3.3.2. Complexation Reactions of Ligands (5-1), (5-3) and (5-4) with $[Rh(cod)Cl]_2$ and $AgClO_4$

Reaction of (**5-1**) with $1/2[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at room temperature gave complex (**5-5**) in high yield (Equation 3-18).

Equation 3-18:

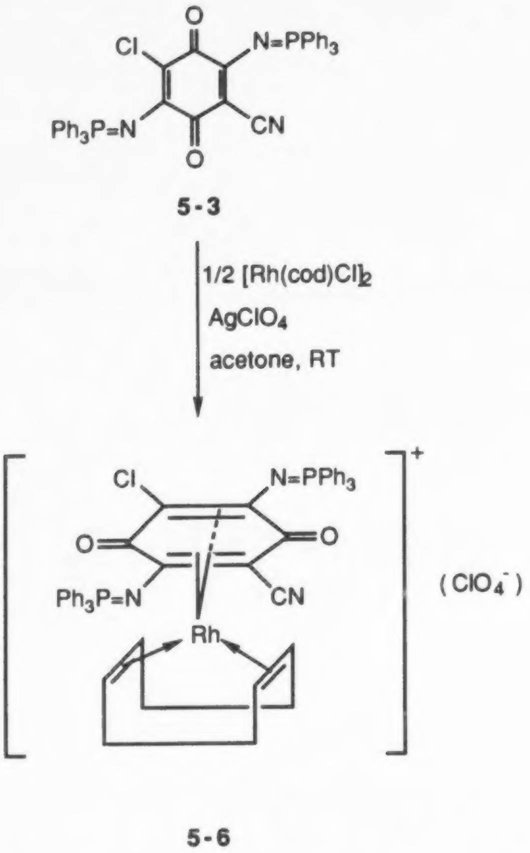

2
O
Cl
N=PPh3
Cl
CN
O
5-1
[Rh(cod)Cl]2
2 AgClO4
acetone
RT
2+
Cl
Cl
O
O
N≡C
N=PPh3
Rh
Rh
C≡N
Ph3P=N
O
O
Cl
Cl
(ClO4-)2

5-5

(FAB) mass spectrum showed a mass peak corresponding to the dinuclear cationic unit of this complex, $[L_2Rh_2(cod)_2]^+$. Other fragments also observed included those which could be derived from a dinuclear complex unit, including $[L_2Rh(cod)]$ and $[LRh(cod)]$. Therefore, it is proposed that this complex is a dimer. The ^{31}P NMR spectrum of the complex showed a single peak at 22.39 ppm, which is about 4 ppm downfield compared with the corresponding ligand. The CN stretching frequency was observed at 2238 cm^{-1}, an increase of about 20 cm^{-1} compared with the corresponding value for the uncoordinated ligand. There are two possible dimeric structures. In one (as shown in Equation 3-18), the imine nitrogen and the nitrogen in CN are σ-coordinated to the Rh center. In this case the antibonding character of the N lone pair would result in an increase in CN stretching frequency upon complexation (see Chapter 2). Alternatively, the quinone oxygen and the imine nitrogen can be σ coordinating centers. Again the uncoordinated CN stretching frequency should increase (see Chapter 2). In the former case, the CO stretching frequencies will not show a big difference between the ligand (**5-1**) and its complex, whereas in the latter case the CO stretching frequencies will be decreased upon complexation because of the π back donation from the Rh center to the CO π^* orbital. The observed CO stretching frequencies for complex (**5-5**) showed no significant difference from the bands of the corresponding ligand (**5-1**). Therefore it is proposed that the structure of (**5-5**) involves coordination to rhodium from the imine nitrogen and the nitrogen of the CN group (Equation 3-18).

Reaction of (**5-3**) with one half equivalent of $[Rh(cod)Cl]_2$ and one equivalent of $AgClO_4$ in acetone at room temperature gave the complex (**5-6**) in high yield (Equation 3-19).

Equation 3-19:



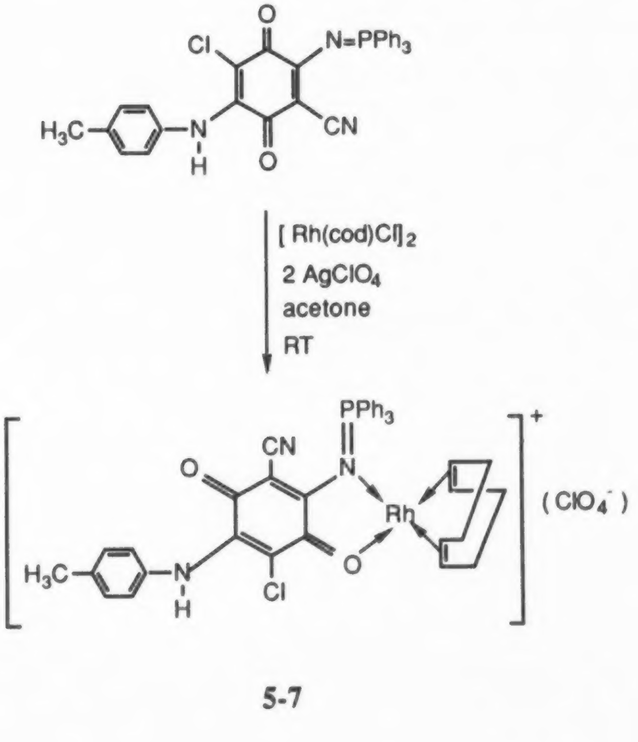
A mass peak correponding to monometallic cation $[LRh(cod)]^+$ of the complex was observed in the mass spectrum (FAB). The elemental analyses data are consistent with the proposed formula. ^{31}P NMR chemical shifts of the complex showed two broad singlets at 17.29 and 21.79 ppm, which are about 1.1 and 3.7 ppm downfield from the signals for the corresponding ligand. The CN stretching frequency was observed at 2229 cm^{-1}, which is an increase of 20 cm^{-1} compared with that of the corresponding ligand, indicating that the CN group either σ-coordinates to the Rh center using the lone pair of the nitrogen to form a dimer as proposed for complex (5-5), or remains a free, uncoordinated group. There is no significant difference for the CO stretching frequencies between the complex (1638 and 1588 cm^{-1}) and the ligand

(1634 and 1589 cm^{-1}), indicating that the oxygen is not coordinated to the Rh center. Therefore, it is proposed that the complex (**5-6**) is a π-coordinated structure.

The reaction of (**5-3**) with $[Rh(cod)Cl]_2$ and two equivalents of $AgClO_4$ in acetone at room temperature was carried out and expected to give a σ-coordinated dinuclear complex. However, the ion of mass $[LRh(cod)]^+$ was observed in the mass spectrum (FAB). The ^{31}P NMR spectrum of the complex shows two singlets at 17.60 and 22.98 ppm, which are very close to the chemical shifts of (**5-6**) (17.29 and 21.79 ppm). The CN stretching frequency was observed at 2232 cm^{-1} which is only 3 cm^{-1} greater than that for (**5-6**). The CO stretching frequencies are also the same as that in (**5-6**). Therefore, it is proposed that this product is actually complex (**5-6**).

Reaction of (**5-4**) with $[Rh(cod)Cl]_2$ and two equivalents of $AgClO_4$ gave the mononuclear complex (**5-7**) in high yield (Equation 3-20).

Equation 3-20:



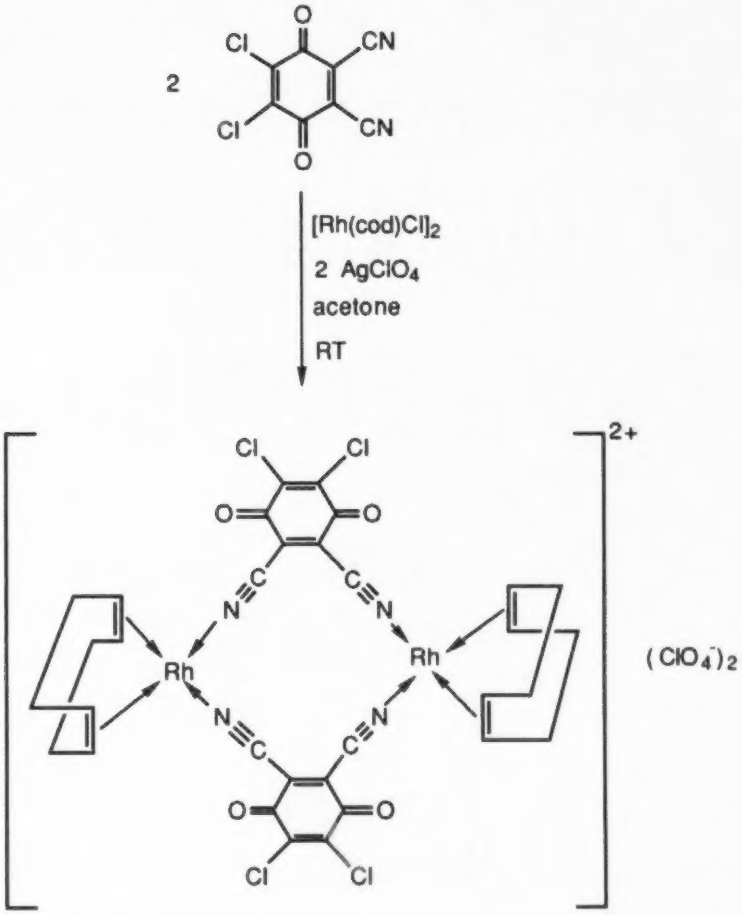
5-7

Two equivalents of Rh precursor were used and it was anticipated that the product could be a dinuclear complex, similar to (**4-12**) - (**4-14**). However, the analytical and spectroscopic data obtained for the product show that it is a mononuclear complex. The monocation $[LRh(cod)]^+$ was observed in the mass spectrum (FAB), but no dinuclear or bis-ligand peaks were observed. The results of elemental analysis are consistent with the proposed formula. The ^{31}P NMR spectrum shows a singlet at 36.72 ppm, which is 17.3 ppm downfield compared with the corresponding ligand. This large shift suggests that the imine nitrogen is coordinated to the Rh center. The ^{1}H NMR data ($\delta_{N\text{-}H}$: 8.30 ppm (s)) and the IR data ($\nu_{N\text{-}H}$: 3239 cm^{-1}) show that the amine nitrogen remains protonated. In the IR spectrum, the CN stretching band for the complex is at 2233 cm^{-1}, which is 19 cm^{-1} higher than that of the corresponding ligand (2214 cm^{-1}).

The parent quinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, reacts with one-half mole equivalent of $[Rh(cod)Cl]_2$ and one equivalent of $AgClO_4$ to form the CN σ-coordinated Rh dimer, (**5-8**) (Equation 3-21).

The ions of mass [RhLRh(cod)], [LRh(cod)] and [LRh] were observed in the mass spectrum (FAB). The stretching frequency of the CN appeared at 2257 cm^{-1} which is about 24 cm^{-1} larger than the corresponding band for the ligand, indicating that the CN is σ coordinated to the Rh center. Since the given ligand geometry does not allow two CN groups to form σ bonds to the same Rh center, it is proposed that this compound is a dimer, as illustrated in Equation 3-19. The ν_{CO} in IR spectrum of the complex appeared at 1702 cm^{-1} which is about a 6 cm^{-1} increase compared with that of the ligand (1696 cm^{-1}) indicating that the oxygen is not coordinated to the Rh center.

Equation 3-21:


2
O
Cl
CN
Cl
CN
O
[Rh(cod)Cl]$_2$
2 AgClO$_4$
acetone
RT
Cl
Cl
O
O
C
N
C
N
Rh
Rh
N
C
N
C
O
O
Cl
Cl
2+
(ClO$_4^-$)$_2$

5-8

3.4. Electrochemistry of *p*-Benzoquinone Derivatives

3.4.1. Results and Discussion

The redox behavior of the internal reference material, Cp_2Fe, was first measured *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with [n-Bu_4N]BF_4 (0.1M) as electrolyte. The CV trace is shown in Figure 3-8.

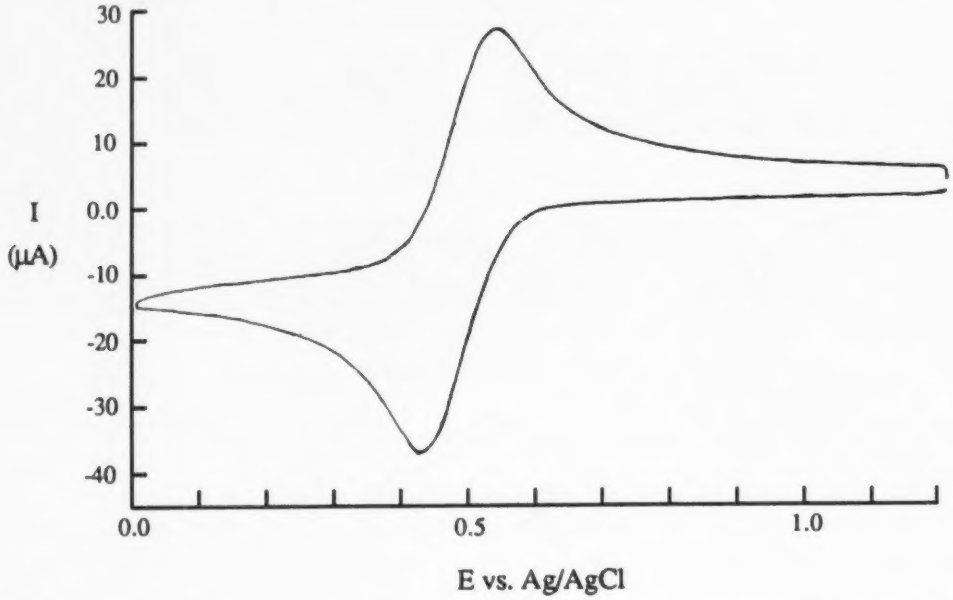


Figure 3-8. Cyclic Voltammetric trace of Cp_2Fe *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with [n-Bu_4N]BF_4 (0.1M) as electrolyte.

From the trace, the following data can be obtained:

$E^{0'} = (0.52 + 0.42)/2 = 0.47$ V

$\Delta E = 0.52 - 0.42 = 0.10$ V = 100 mV

$i_{p,c} / i_{p,a} = i_{p,c'} / i_{p,a} + 0.485 \times i_{s,p} / i_{p,a} + 0.086$

$= 26/(-37) + 0.485 \times (-15)/ (-37) + 0.086$

$= 1.0$

These data are consistent with those given in reference[168] in which the $E^{0'} = 0.47$ V *vs* s.c.e., $\Delta E = 60$ mV and $i_{p,c} / i_{p,a} = 1.0$. The only difference is that in our system, the value for ΔE (100 mV) is larger than the value (60 mV) for the s.c.e. system, but it does not influence the average position ($E^{0'}$) of the anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) values.

The reduction potentials of some other known compounds have been measured and the data are listed in Table 3-8. For example, the CV trace for tetrachloro-*p*-benzoquinone shown in Figure 3-9.

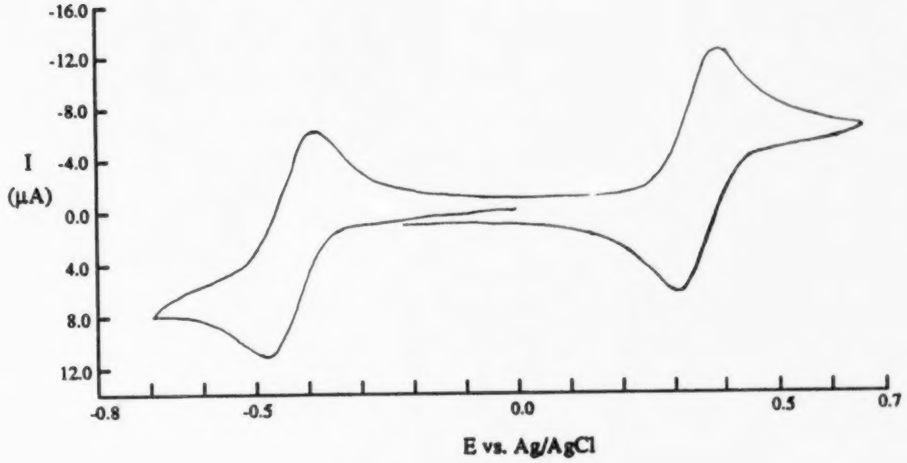


Figure 3-9. Cyclic Voltammetric trace of tetrachloro-*p*-benzoquinone *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with $[n\text{-}Bu_4N]BF_4$ (0.1M) as electrolyte.

From the trace the following data can be obtained:

$E_1{}^{0'} = (0.30 + 0.38)/2 = 0.34$ V, $\Delta E_1 = 0.38 - 0.30 = 0.08$ V $= 80$ mV

$E_2{}^{0'} = (-0.38 + (-0.48))/2 = -0.43$ V, $\Delta E_2 = (-0.38)-(-0.43) = 100$ mV

These data are consistent with those given in reference[64] in which $E^{0'} = +0.35$ and -0.43 V *vs* Ag/AgI in CH_2Cl_2 at 25 °C with $[n\text{-}Bu_4N]ClO_4$ (0.5 M) as electrolyte.

The electrochemical data for the monosubstituted phosphinimine derivatives show that they reversibly accept two electrons. Some examples are shown as follows.

The CV trace of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (**3-2**) is shown in Figure 3-10.

$E_1^{0'} = ((-0.05) + (-0.16))/2 = -0.11$ V, $\Delta E_1 = (-0.05)-(-0.16) = 110$ mV

$E_2^{0'} = ((-0.78) + (-0.90))/2 = -0.84$ V, $\Delta E_2 = (-0.78)-(-0.90) = 120$ mV

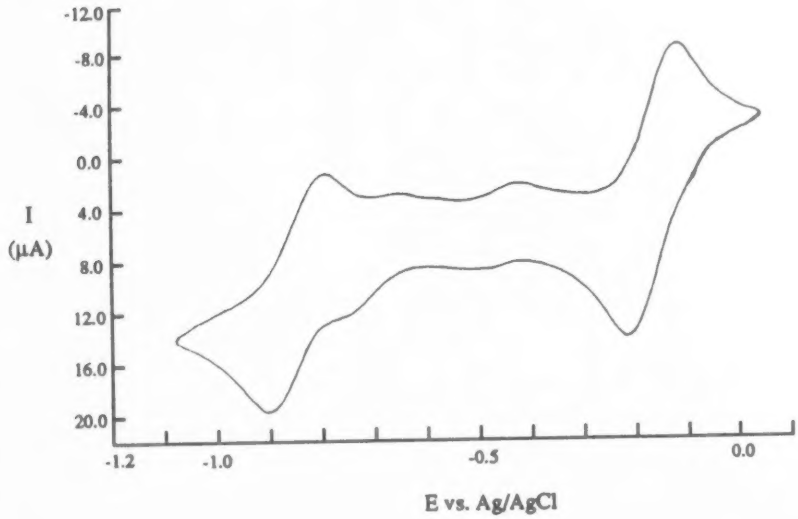


Figure 3-10. Cyclic Voltammetric trace of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)*p*-benzoquinone (**3-2**) *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with $[n\text{-}Bu_4N]BF_4$ (0.1M) as electrolyte.

The CV trace of 3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (**5-1**) is shown in Figure 3-11.

$E_1{}^{0'} = (0.08 - 0.04)/2 = 0.02$ V, $\Delta E_1 = (0.08)+(0.04) = 120$ mV

$E_2{}^{0'} = ((-0.65) + (-0.80))/2 = -0.73$ V, $\Delta E_2 = (-0.65)-(-0.80) = 150$ mV

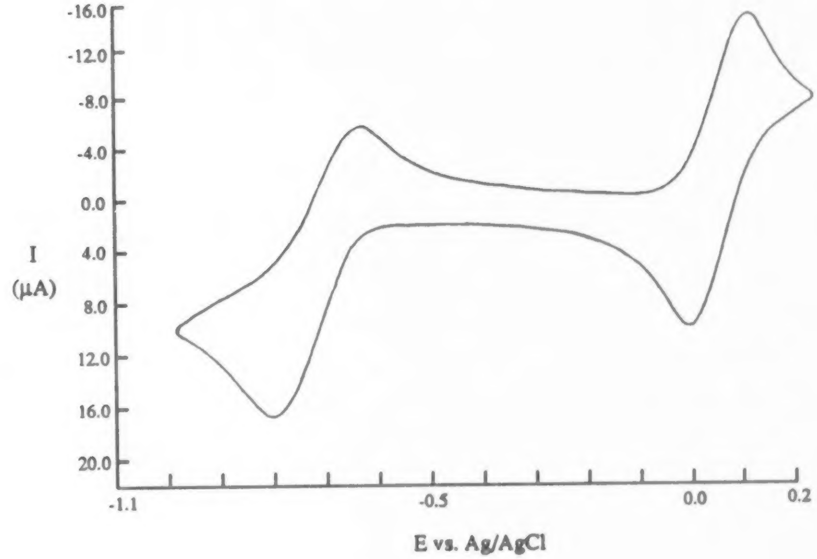


Figure 3-11. Cyclic Voltammetric trace of 3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (**5-1**) *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with $[n\text{-}Bu_4N]BF_4$ (0.1M) as electrolyte.

An unusual observation is that the CV trace of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (**3-1**) consists of four pairs of peaks instead of the expected two pairs of peaks. (Figure 3-12)

From the trace, the following data are obtained:

$E_1^{0'} = (0.08 - 0.03)/2 = 0.03$ V, $\Delta E_1 = (0.08)-(-0.03) = 110$ mV

$E_2^{0'} = ((-0.61) + (-0.50))/2 = -0.56$ V, $\Delta E_2 = (-0.50)-(-0.61) = 110$ mV

$E_3^{0'} = ((-0.78) + (-0.68))/2 = -0.73$ V, $\Delta E_3 = (-0.68)-(-0.78) = 100$ mV

$E_4^{0'} = ((-1.19) + (-1.07))/2 = -1.13$ V, $\Delta E_4 = (-1.07)-(-1.19) = 120$ mV

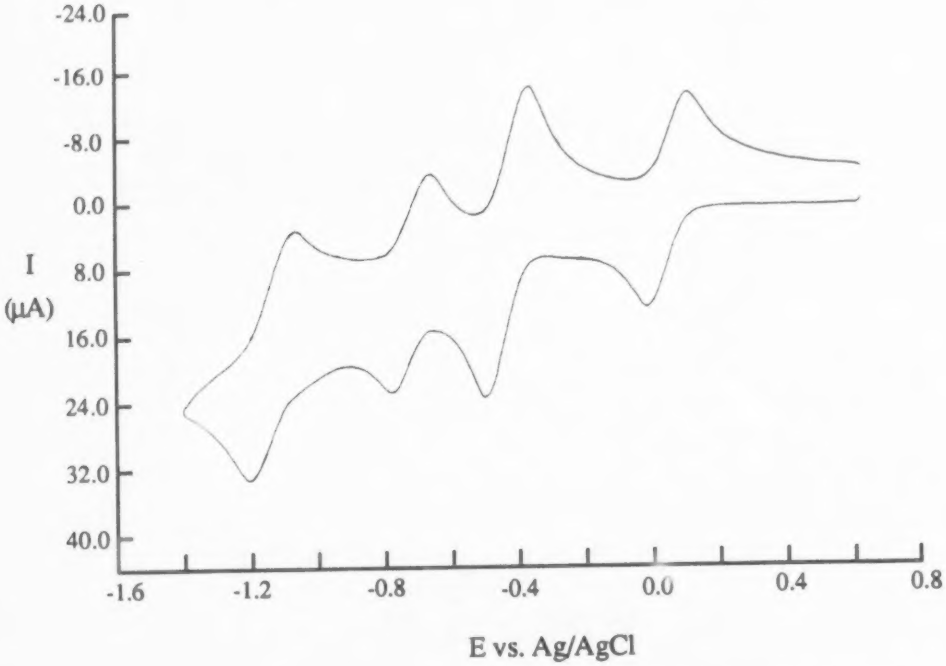


Figure 3-12. Cyclic Voltammetric trace of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (**3-1**) *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with [n-Bu_4N]BF_4 (0.1M) as electrolyte.

It is not likely that this compound can accept four electrons. This has been confirmed by the experiment using the same molarity of Cp_2Fe as used for the measurement of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone. The result showed that the magnitude of the peak of the Cp_2Fe is almost twice as big as those for 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone. This means that each pair of peaks in the spectrum of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone does not represent a one electron reduction. It seems likely that there are two species present in this system. Comparing the data with that of (**3-1**), (**3-2**), (**3-4**), (**3-5**) and (**5-1**), it is suggested that the data of $E^{o'}$ = +0.03 and -0.73 V correspond to compound (**3-3**) whereas -0.56 and -1.13 V correspond to the unknown compound.

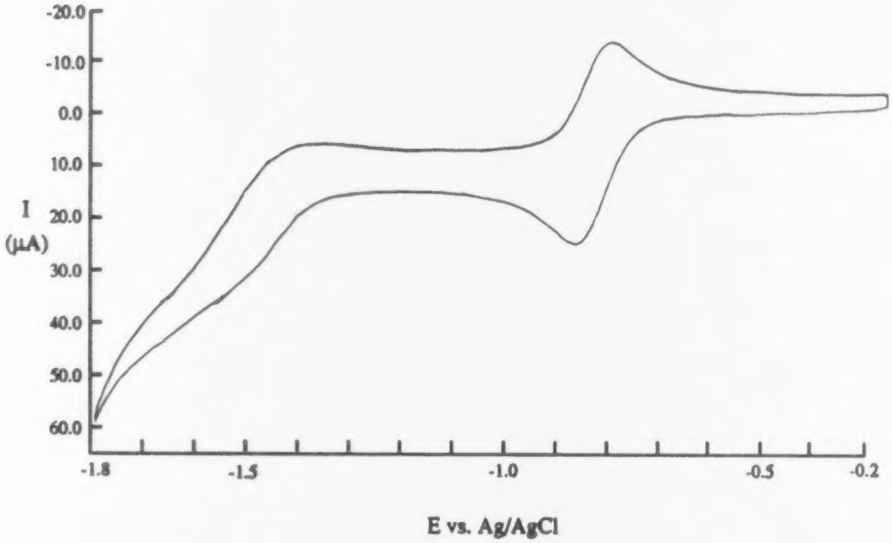


Figure 3-13. Cyclic Voltammetric trace of 3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (**5-3**) *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with $[n\text{-}Bu_4N]BF_4$ (0.1M) as electrolyte.

The CV trace for each of the disubstituted phosphinimine derivatives shows that the compound can accept the first electron reversibly and accept the second electron irreversibly. One representative example, the CV trace of 3-cyano-6-chloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone (**5-3**), is shown in Figure 3-13.

$E_1^{0'} = ((-0.82) + (-0.89))/2 = -0.86$ V, $\Delta E_1 = (-0.82)-(-0.89) = 70$ mV

For the phosphinimine and aniline disubstituted derivatives, the traces show that both pairs of peaks are reversible. The CV trace of one representative example, 3,6-dichloro-5-(*p*-fluoro-phenylamino)-2-(triphenylphosphinimino)-*para*-benzoquinone (**4-1**), is shown in Figure 3-14. The data obtained from Figure 3-14 are as follows.

$E_1^{0'} = ((-0.74) + (-1.00))/2 = -0.87$ V, $\Delta E_1 = (-0.74)-(-1.00) = 260$ mV

$E_2^{0'} = ((-1.32) + (-1.65))/2 = -1.49$ V, $\Delta E_2 = (-1.32)-(-1.65) = 330$ mV

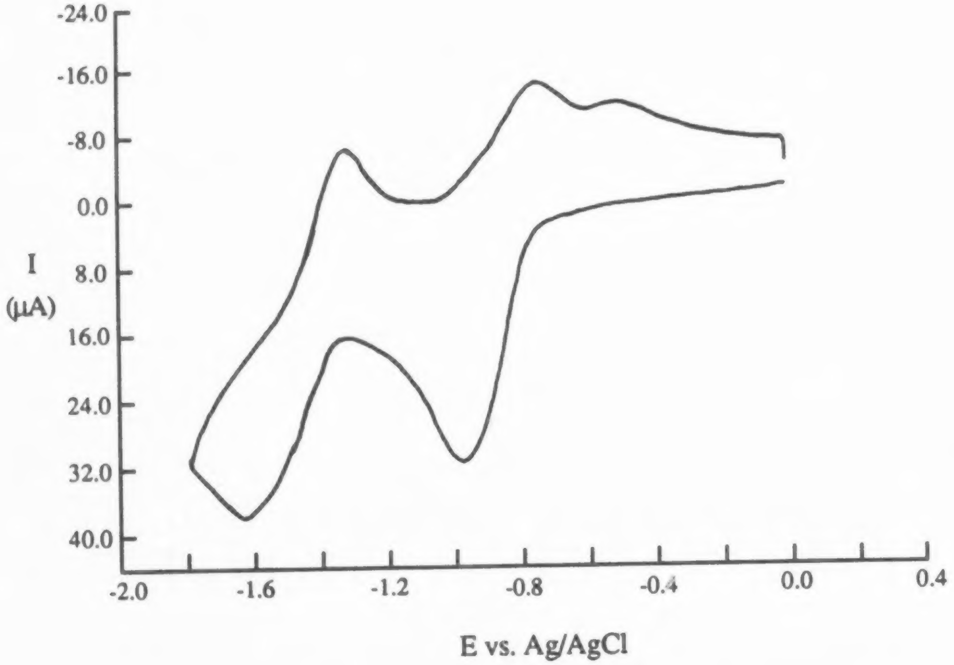


Figure 3-14. Cyclic Voltammetric trace of 3,6-dichloro-5-(*p*-fluoro-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone (**4-1**) *vs* Ag/AgCl at 23 °C in CH_2Cl_2 with $[n\text{-}Bu_4N]BF_4$ (0.1M) as electrolyte.

Most metal complexes of the quinone derivatives afford voltagrams which are not reversible during the reduction. In contrast, the electrochemical data for the complex, [(3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone) {σ-O, N} Rh(cod)](ClO$_4$), showed that both pairs of peaks are reversible. The CV trace of [(3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone) {σ-O, N} Rh(cod)](ClO$_4$) (**3-19**) is shown in Figure 3-15.

$E_1^{0'} = ((-0.38) + (-0.45))/2 = -0.42$ V, $\Delta E_1 = (-0.38)-(-0.45) = 70$ mV

$E_2^{0'} = ((-1.05) + (-1.14))/2 = -1.10$ V, $\Delta E_2 = (-1.05)-(-1.14) = 90$ mV

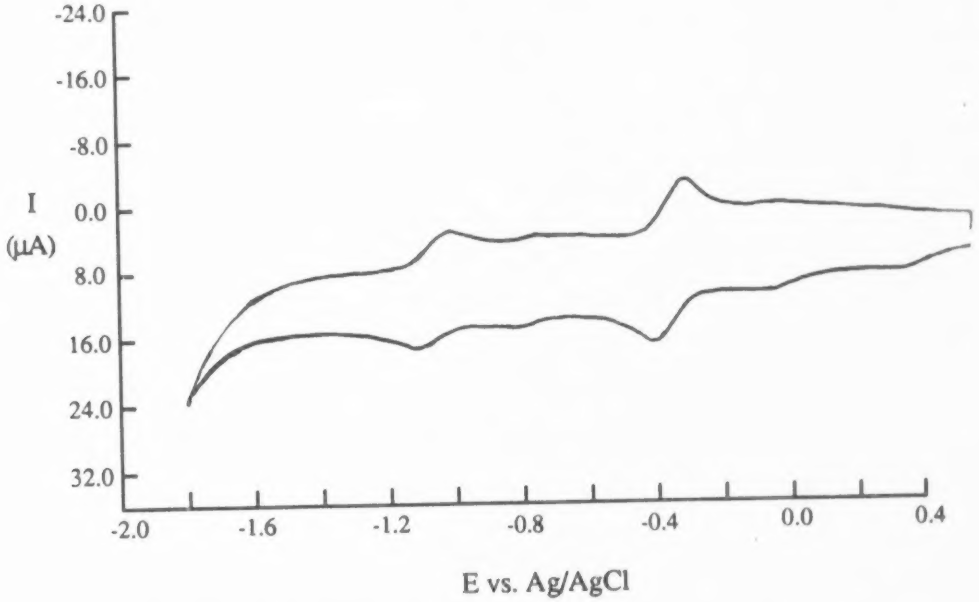


Figure 3-15. Cyclic Voltammetric trace of [(3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone) {σ-O, N} Rh(cod)](ClO$_4$) (**3-19**) *vs* Ag/AgCl at 23 °C in CH$_2$Cl$_2$ with [n-Bu$_4$N]BF$_4$ (0.1M) as electrolyte.

Table 3-1. Phosphorus-31 NMR[a] Data and UV Spectra Data for Compounds (**3-1**) - (**3-26**).

Compounds	**No.**	**δP** (ppm)	**λ_{max}** (nm)	**log ε**
3,5,6-trifluoro-2-(triphenylphosphinimino)-*p*-benzoquinone	**3-1**	15.27(s)	544	3.61
3,5,6-trifluoro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-2**	16.56(s)	536	3.47
3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone	**3-3**	14.44(s)	570	3.46
3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-4**	15.42(s)	572	3.46
3,5,6-trichloro-2-(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-5**	19.52(s)	554	3.12
3,6-difluoro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone	**3-6**	14.74(s)	386	4.58
3,6-difluoro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-7**	16.46(s)	386	4.48
3,6-difluoro-2,5-bis(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-8**	20.86(s)	380	4.38

Table 3-1. continued

Compounds	No.	δP (ppm)	λ_{max} (nm)	log ε
3,6-difluoro-2,5-[N=P(Ph)$_2$CH$_2$P(Ph)$_2$]$_2$-*p*-benzoquinone	**3-9**	-29.68(d)(P^{III})^b 15.31(d)(P^V)^b	393	4.52
3,6-dichloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone	**3-10**	15.02(s)	388	4.19
3,6-dichloro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-11**	15.50(s)	388	4.21
3,6-difluoro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-12**	15.13(s) 16.08(s)	385	4.27
3,6-difluoro-2-(triphenylphosphinimino)-5-(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-13**	15.20(s) 20.13(s)	383	4.47
3,6-difluoro-2-(methyldiphenylphosphinimino)-5-(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-14**	16.48(s) 20.54(s)	382	4.24

Table 3-1. continued

Compounds	No.	δP (ppm)	λmax (nm)	log ε
3,6-difluoro-2-[N=P(Ph)$_2$CH$_2$P(Ph)$_2$]-5-(triphenylphosphinimino)-*p*-benzoquinone	**3-15**	-29.46(d)(P^{III})^c 15.24(d)(PPh$_2$)^c 14.50(s)(PPh$_3$)	388	4.35
3,6-dichloro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-16**	15.12(s) 15.56(s)	388	4.25
Bis(diphenyl [N, N'-2,5-difluoro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dinone]iminophosphino) methane	**3-17**	6.47(s)(PPh$_2$) 14.66(s)(PPh$_3$)	396	4.70
[(3,5,6-trifluoro-2-(triphenylphosphinimino)-*p*-benzoquinone)-{σ-O, N} Rh(cod)](ClO$_4$)	**3-18**	39.2(s)	546	3.20
[(3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone) {σ-O, N} Rh(cod)](ClO$_4$)	**3-19**	31.19(s)	550	3.21

Table 3-1. continued

Compounds	No.	δP (ppm)	λmax (nm)	log ε
[π-(3,6-difluoro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO_4)	**3-20**	24.98(s)	400 574	4.47 3.85
[π-(3,6-difluoro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO_4)	**3-21**	28.19(s)	400 564	4.03 3.72
[π-(3,6-difluoro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO_4)	**3-22**	24.99(s) 28.14(s)	448 565	3.97 3.57
[π-(3,6-dichloro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO_4)	**3-23**	24.30(s) 27.19(s)	400 566	4.04 3.63

Table 3-1. continued

Compounds	No.	δP (ppm)	λ_{max} (nm)	log ε
{π, π'-[Bisdiphenyl (N, N'-2,5-difluoro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dinone)iminophosphino methane]-$Rh_2(cod)_2$}$(ClO_4)_2$	**3-24**	18.85(s)(PPh_2) 24.78(s)(PPh_3)	408 576	4.41 4.00
3-chloro-2-(triphenylphosphinimino)-*p*-naphthoquinone	**3-25**	13.41(s)	486	3.40
3-chloro-2-(methyldiphenylphosphinimino)-*p*-naphthoquinone	**3-26**	14.21(s)	490	3.45

[a] Spectra obtained in $CDCl_3$ solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to lowfield of standard.

[b] $^2J_{PP} = 52.90$ Hz. [c] $^2J_{PP} = 52.70$ Hz.

Table 3-2. Phosphorus-31 NMR^a Data, ^{1}H NMR^b data and IR^c data for compounds (**4-1**) - (**4-23**).

Compound		δ P (ppm)	δ H(N-H) (ppm)	$\nu_{(N-H)}$ (cm^{-1})	λ_{max} (nm)	log ε
3,6-dichloro-5-(*p*-fluorophenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA1)	**4-1**	15.86(s)	8.25(s)	3235	381	4.42
3,6-dichloro-5-(*p*-chlorophenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA2)	**4-2**	15.94(s)	8.25(s)	3220	387	4.42
3,6-dichloro-5-(*p*-methylphenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA3)	**4-3**	15.84(s)	8.32(s)	3251	385	4.30

Table 3-2. continued

Compound		δ P (ppm)	δ H(N-H) (ppm)	$\nu_{(N\text{-}H)}$ (cm^{-1})	λ_{max} (nm)	log ε
3,6-dichloro-5-(*p*-NH_2-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA4)	**4-4**	15.67(s)	8.30(s)	3263	371	4.00
3,6-dichloro-5-(*p*-fluorophenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA5)	**4-5**	17.06(s)	8.35(s)	3244	374	4.26
3,6-dichloro-5-(*p*-chlorophenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA6)	**4-6**	17.08(s)	8.30(s)	3235	379	4.17

Table 3-2. continued

Compound		δ P (ppm)	δ H(N-H) (ppm)	$\nu_{(N-H)}$ (cm^{-1})	λ_{max} (nm)	log ε
3,6-dichloro-5-(*p*-methylphenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA7)	**4-7**	16.94(s)	8.37(s)	3251	380	4.25
3,6-dichloro-5-(*p*-NH_2-phenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA8)	**4-8**	16.86(s)	8.37(s)	3224	366	4.05
1,4-N,N'-bis(2,5-dichloro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dione)-phenyldiamine, (H_2QA9)	**4-9**	15.81(s)	8.32(s)	3264	377	4.47

Table 3-2. continued

Compound		δ P (ppm)	δ H(N-H) (ppm)	$\nu_{(N\text{-}H)}$ (cm^{-1})	λ_{max} (nm)	log ε
2-(triphenylphosphinimino)-3,5-bis(3,5-dimethylpyrazol-1-yl)-6-chlorobenzoquinone	**4-10**	14.89(s)	-	-	396	3.50
3-chloro-2-(triphenyl-phosphinimino)-10H-5-thia-10-azaanthracene-1,4-dione	**4-11**	15.71(s)	8.25(s)	3274	458	4.98
[(QA1) {σ-O, N=PPh$_3$} Rh$_2$(cod)$_2$](ClO$_4$)	**4-12**	29.45(s)	-	-	454	3.19
[(QA2) {σ-O, N=PPh$_3$} Rh$_2$(cod)$_2$](ClO$_4$)	**4-13**	30.20(s)	-	-	434	3.06
[(QA3) {σ-O, N=PPh$_3$} Rh$_2$(cod)$_2$](ClO$_4$)	**4-14**	30.00(s)	-	-	442	2.78
[(HQA3) {σ-O, N=PPh$_3$} Rh(cod)](ClO$_4$)	**4-15**	31.20(s)	8.00(s)	3267	435	2.98

Table 3-2. continued

Compound		δ P (ppm)	δ H(N-H) (ppm)	$\nu_{(N\text{-}H)}$ (cm^{-1})	λ_{max} (nm)	log ε
3,6-difluoro-2,5-bis(*p*-fluorophenylamino)-*p*-benzoquinone	**4-16**	-	9.15(s)	3230	398	4.23
3,6-difluoro-2,5-bis(*p*-chlorophenylamino)-*p*-benzoquinone	**4-17**	-	9.22(s)	3237	406	4.27
3,6-difluoro-2,5-bis(*p*-bromophenylamino)-*p*-benzoquinone	**4-18**	-	9.20(s)	3232	400	4.26
3,6-difluoro-2,5-bis(*p*-iodophenylamino)-*p*-benzoquinone	**4-19**	-	9.17(s)	3242	410	4.20
3,6-difluoro-2,5-bis(*p*-methylphenylamino)-*p*-benzoquinone	**4-20**	-	9.03(s)	3246	416	4.19

Table 3-2. continued

Compound		δ P (ppm)	δ H(N-H) (ppm)	$\nu_{(N\text{-}H)}$ (cm^{-1})	λ_{max} (nm)	log ε
3,6-difluoro-2,5-bis(phenylamino)-*p*-benzoquinone	**4-21**	-	9.12(s)	3248	402	4.31
3,6-difluoro-2,5-bis(*p*-nitrophenylamino)-*p*-benzoquinone	**4-22**	-	9.67(s)	3257	416	4.52
3,6-difluoro-2,5-bis(*p*-NMe$_2$-phenylamino)-*p*-benzoquinone	**4-23**	-	8.97	3278	522	4.15

[a] Spectra obtained in CDCl$_3$ solution; ppm vs 85% H$_3$PO$_4$. Positive values indicate resonance to lowfield of standard.

[b] Spectra obtained in CDCl$_3$ solution; ppm vs Me$_4$Si. [c] All IR samples were run in CH$_2$Cl$_2$.

Table 3-3. Summary of Crystallographic Data of Compound (**4-3**).

Compound	(**4-3**)
Formula	$C_{31.5}H_{24}Cl_3N_2O_2P$
formula weight	599.85
crystal size (mm)	0.50 x 0.15 x 0.02
space group	*C*2/*c*(No. 15)
crystal system	monoclinic
unit cell parameters[a]	
a (Å)	27.705(2)
b (Å)	9.410(1)
c (Å)	22.920(1)
β (deg)	107.15(1)
V (Å^3)	5709.6(8)
Z	8
ρ_{calcd} (g/cm^3)	1.396
μ (mm^{-1})	3.699
diffractometer[141]	Siemens P4/RA[b]
radiation (λ, [Å])	Cu Kα (1.54178)
Temperature (°C)	22
scan type	θ-2θ
maximum 2θ (deg)	110.0
total data collected	3666
independent reflections	3581
structure solution method	direct methods (*SHELXS-86*[c])
refinement method	full-matrix least-squares on F^2[d]

Table 3-3. continued

compound	**(4-3)**
absorption correction method	*DIFABS*[e]
range of abs. corr. factors	1.185-0.793
restraints/parameters (*NV*)	2[f]/353
goodness-of-fit (*S*)[g]	1.043 $[F_o^2 \geq -3\sigma(F_o^2)]$
final R indices[h]	
$F_o^2 > 2\sigma(F_o^2)$	$R_1 = 0.0784$, $wR_2 = 0.1983$
all data	$R_1 = 0.1147$, $wR_2 = 0.2320$

[a] Obtained from least-squares refinement of 25 reflections with 53.0° < 2θ < 58.0°

[b] Programs for diffractometer operation and data collection and reduction were those of the *XSCANS* system supplied by Siemens.

[c] Sheldrick, G. M. *Acta Crystallogr.* 1990, *A46*, 467.

[d] Sheldrick, G. M. *J. Appl. Cryst.*, in preparation. refinement on F_o^2 for ALL reflections (all of these having $F_o^2 < -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[f] Restraints were applied to fix distances within the CH_2Cl_2 solvent molecule: Cl3-C91 distance = 1.80Å and Cl3-Cl3' = 3.00Å.

[g] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.111P)^2 + 42.0593P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3)$.

[h] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

Table 3-4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters[a,b] for (**4-3**).

Atom	x	y	z	U_{eq}, (Å^2)
Cl1	0.16268(7)	0.0052(2)	-0.13858(8)	0.0518(6)*
Cl2	0.36607(7)	0.1179(2)	-0.20236(9)	0.0550(6)*
Cl3	-0.0100(2)	0.4028(5)	0.1824(2)	0.265(4)*
P	0.36307(7)	-0.1755(2)	-0.04707(8)	0.0392(5)*
O1	0.2623(2)	-0.1121(5)	-0.0815(2)	0.0465(13)*
O2	0.2647(2)	0.2321(6)	-0.2640(3)	0.067(2)*
N1	0.3523(2)	-0.0795(6)	-0.1078(3)	0.0433(15)*
N2	0.1763(2)	0.1799(6)	-0.2509(3)	0.050(2)*
C1	0.2162(2)	0.0286(7)	-0.1625(3)	0.038(2)*
C2	0.2611(2)	-0.0380(7)	-0.1262(3)	0.036(2)*
C3	0.3103(2)	-0.0158(7)	-0.1406(3)	0.036(2)*
C4	0.3095(3)	0.0769(7)	-0.1877(3)	0.038(2)*
C5	0.2655(3)	0.1456(7)	-0.2234(3)	0.042(2)*
C6	0.2155(3)	0.1113(7)	-0.2111(3)	0.039(2)*
C11	0.1246(3)	0.1401(8)	-0.2697(3)	0.045(2)*
C12	0.1106(3)	0.0001(8)	-0.2788(3)	0.051(2)*
C13	0.0589(3)	-0.0328(9)	-0.3028(3)	0.057(2)*
C14	0.0227(3)	0.0713(10)	-0.3172(3)	0.055(2)*
C15	0.0381(3)	0.2102(10)	-0.3074(4)	0.063(2)*
C16	0.0886(3)	0.2459(9)	-0.2845(4)	0.057(2)*
C17	-0.0327(3)	0.0354(12)	-0.3434(4)	0.077(3)*
C21	0.3562(3)	-0.0811(8)	0.0188(3)	0.043(2)*
C22	0.3556(3)	0.0651(8)	0.0165(4)	0.052(2)*
C23	0.3535(3)	0.1433(10)	0.0671(4)	0.068(2)*

Table 3-4. continued

Atom	x	y	z	U_{eq}, (Å^2)
C24	0.3517(4)	0.0767(13)	0.1189(5)	0.086(3)*
C25	0.3513(4)	-0.0711(13)	0.1217(4)	0.082(3)*
C26	0.3544(3)	-0.1497(3)	0.0716(3)	0.063(2)*
C31	0.3352(3)	-0.3492(7)	-0.0545(3)	0.038(2)*
C32	0.2969(3)	-0.3900(8)	-0.0292(4)	0.048(2)*
C33	0.2775(3)	-0.5252(9)	-0.0386(4)	0.057(2)*
C34	0.2932(3)	-0.6198(9)	-0.0742(4)	0.067(2)*
C35	0.3297(4)	-0.5821(9)	-0.1000(4)	0.071(3)*
C36	0.3512(3)	-0.4473(9)	-0.0900(3)	0.055(2)*
C41	0.4303(3)	-0.2076(8)	-0.0280(3)	0.045(2)*
C42	0.4529(3)	-0.3058(11)	0.0172(4)	0.078(3)*
C43	0.5044(3)	-0.3302(12)	0.0328(5)	0.086(3)*
C44	0.5330(3)	-0.2581(11)	0.0043(4)	0.069(2)*
C45	0.5118(3)	-0.1618(10)	-0.0401(4)	0.071(3)*
C46	0.4602(3)	-0.1372(9)	-0.0565(3)	0.051(2)*
C91	0.00	0.3025(21)	0.25	0.250

[a] Numbers in parentheses are estimated stardard deviations in the least significant digits. [b] Anisotropically refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. Parameters without an e.s.d. were not refined.

Table 3-5. Selected Bond Distances (Å) in compound (**4-3**).

Cl1-C1	1.740(7)	N2-C6	1.358(9)
Cl2-C4	1.741(7)	N2-C11	1.419(9)
P-N1	1.612(6)	C1-C2	1.423(9)
P-C21	1.809(7)	C1-C6	1.353(9)
P-C31	1.795(7)	C2-C3	1.510(9)
P-C41	1.809(7)	C3-C4	1.382(9)
O1-C2	1.230(7)	C4-C5	1.408(10)
O2-C5	1.231(8)	C5-C6	1.527(10)
N1-C3	1.327(8)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3-6. Selected Bond Angles (deg) in the compound (**4-3**).

N1-P-C21	114.0(3)	Cl2-C4-C3	118.8(5)
N1-P-C31	117.6(3)	Cl2-C4-C5	117.3(5)
N1-P-C41	102.6(3)	C3-C4-C5	123.8(6)
C21-P-C31	112.2(3)	O2-C5-C4	124.2(7)
C21-P-C41	104.8(3)	O2-C5-C6	117.7(7)
C31-P-C41	104.8(3)	C4-C5-C6	118.1(6)
P-N1-C3	130.7(5)	N2-C6-C1	129.7(6)
C6-N2-C11	127.9(6)	N2-C6-C5	111.4(6)
C2-C1-C6	122.1(6)	C1-C6-C5	118.8(6)
Cl1-C1-C2	116.0(5)	N2-C11-C12	121.0(7)
Cl1-C1-C6	121.8(5)	N2-C11-C16	118.4(7)
O1-C2-C1	122.8(6)	P-C21-C22	117.5(6)
O1-C2-C3	117.1(6)	P-C21-C26	122.7(6)
C1-C2-C3	120.0(6)	P-C31-C32	124.5(5)
N1-C3-C2	120.6(6)	P-C31-C36	117.3(5)
N1-C3-C4	122.5(6)	P-C41-C42	119.7(6)
C2-C3-C4	116.8(6)	P-C41-C46	122.0(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3-7. Phosphorus-31 NMR[a] Data, ^{1}H NMR[b] Data and IR[c,d] Data for Ccompounds (**5-1**) - (**5-8**).

Compound		δ P (ppm)	δ $H_{(N-H)}$ (ppm)	ν_{CN} (cm^{-1})	ν_{N-H} (cm^{-1})	λ_{max} (nm)	log ε
3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone	**5-1**	18.45(s)	------	2218	------	524	3.57
3-cyano-5,6-dichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**5-2**	19.66(s)	------	2212	------	528	3.55
3-cyano-6-chloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone	**5-3**	16.20(s)	------	2209	------	390	4.51
3-cyano-6-chloro-5-(*p*-methyl-phenylamino)-2-(triphenyl-phosphinimino)-*p*-benzoquinone	**5-4**	19.43(s)	8.40(s)	2214	3250	376	4.12
[(3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone) σ-{N, N} Rh(cod)]$_2$(ClO$_4$)$_2$	**5-5**	22.39(s)	------	2238	------	518	3.90

Table 3-7. continued

Compound		δ P (ppm)	δ $H_{(N\text{-}H)}$ (ppm)	ν_{CN} (cm^{-1})	$\nu_{N\text{-}H}$ (cm^{-1})	λ_{max} (nm)	log ε
[π-(3-cyano-6-chloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO_4)	**5-6**	17.29(s) 21.79(s)	------	2229	------	393	4.47
[(3-cyano-6-chloro-5-(*p*-mrthyl-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone)-{σ-O, N=PPh_3} Rh(cod)](ClO_4)	**5-7**	36.72(s)	8.30(s)	2233	3239	377	4.09
[(2,3-dichloro-5,6-dicyano-1,4-benzoquinone)$_2$-{σ-N, N} $Rh_2(cod)_2$](ClO_4)$_2$	**5-8**	------	------	2257	------	353	4.12

[a] Spectra obtained in $CDCl_3$ solution; ppm vs 85% H_3PO_4. Positive values indicate resonance to lowfield of standard.

[b] Spectra obtained in $CDCl_3$ solution; ppm vs Me_4Si. [c] All IR samples were run in microscope.

[d] The parent quinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, ν_{CN} = 2233 cm^{-1}.

Table 3-8. Reduction Potential ($E^{0'}$) Data of the Quinone Derivatives.

Compound	No.	$E^{0'}$(V)
p-benzoquinone[a]		-0.10 -0.85
tetrachloro-*p*-benzoquinone[b]		+0.34 -0.43
2,3-dichloro-1,4-naphthoquinone[c]		-0.34 -0.96
2-chloro-3-(triphenylphosphinimino)-1,4-naphthoquinone	**3-25**	-0.39 -1.02
2-chloro-3-(methyldiphenylphosphinimino)-1,4-naphthoquinone	**3-26**	-0.40 -1.03
3,5,6-trifluoro-2-(triphenylphosphinimino)-*p*-benzoquinone	**3-1**	0.00 -0.76
3,5,6-trifluoro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-2**	-0.05 -0.79
3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone[d]	**3-3**	+0.03 -0.73
3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-4**	-0.11 -0.84

Table 3-8. continued

Compound	No.	$E^{0'}$(V)
3,5,6-trichloro-2-(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-5**	-0.14 -0.88
3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone	**5-1**	+0.02 -0.73
3-cyano-5,6-dichloro-2-(dimethylphenylphosphinimino)-*p*-benzoquinone	**5-2**	-0.06 -0.76
3,6-dichloro-5-(*p*-fluoro-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone	**4-1**	-0.87 -1.49
3,6-dichloro-5-(*p*-chloro-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone	**4-2**	-0.84 -1.50
3,6-dichloro-5-(*p*-methyl-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone	**4-3**	-0.79 -1.47
3,6-dichloro-5-(*p*-NH_2-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone	**4-4**	-0.86 -1.37
3,6-dichloro-5-(*p*-fluoro-phenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**4-5**	-0.83 -1.54

Table 3-8. continued

Compound	No.	$E^{0'}$(V)
3,6-dichloro-5-(*p*-chloro-phenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**4-6**	-0.83 -1.51
3,6-dichloro-5-(*p*-methyl-phenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**4-7**	-0.91 -1.57
3,6-dichloro-5-(*p*-NH_2-phenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone	**4-8**	-0.85 -1.49
1,4-N,N'-bis[2,5-dichloro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dinone]-phenyldiamine	**4-9**	-0.89 -1.51
3-chloro-2-(triphenylphosphinimino)-10H-5-thia-10-azaanthracene-1,4-dione	**4-11**	-0.76 -1.37
3,6-difluoro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone	**3-6**	-0.66
3,6-difluoro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-7**	-0.68
3,6-difluoro-2,5-bis(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-8**	-0.69

Table 3-8. continued

Compound	No.	$E^{0'}$(V)
3,6-difluoro-2,5-[N=P(Ph)$_2$CH$_2$PPh$_2$]$_2$-*p*-benzoquinone	**3-9**	-0.72
3,6-difluoro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-12**	-0.67
3,6-difluoro-2-(triphenylphosphinimino)-5-(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-13**	-0.68
3,6-difluoro-2-(methyldiphenylphosphinimino)-5-(dimethylphenylphosphinimino)-*p*-benzoquinone	**3-14**	-0.68
3,6-difluoro-2-[N=P(Ph)$_2$CH$_2$PPh$_2$]-5-(triphenylphosphinimino)-*p*-benzoquinone	**3-15**	-0.67
3,6-dichloro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone	**3-16**	-0.87
3-cyano-6-chloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone	**5-3**	-0.86
Bisdiphenyl (N, N'-2,5-difluoro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dinone)iminophosphorane methane	**3-17**	-0.73

Table 3-8. continued

Compound	No.	$E^{0'}$(V)
[π-(3,6-dichloro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO_4)	**3-23**	-0.18 -0.90
[(3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone) {σ-O, N} Rh(cod)](ClO_4)	**3-19**	-0.44 -1.12

[a] Reference data[56] gave: $E^{0'}$ = -0.15 and -0.81 V *vs* Ag/AgCl in DMF at 19 °C with [n-Bu_4N]ClO_4 (0.1 M)as electrolyte.

[b] Reference data[56] gave: $E^{0'}$ = +0.35 and -0.43 V *vs* Ag/AgI in CH_2Cl_2 at 25 °C with [n-Bu_4N]ClO_4 (0.5 M) as electrolyte.

[c] Reference data[56] gave: $E^{0'}$ = -0.31 and -0.96 V *vs* Ag/AgCl in DMF at 19 °C with [n-Et_4N]ClO_4 (0.1 M) as electrolyte.

[d] The potential of another two pairs of peaks: $E^{0'}$ = -0.56 and -1.13 V.

Chapter 4

Phosphinimine and 3,5-Dimethylpyrazole Derivatives of Cyanuric Chloride or Halogenated Pyrimidine, and Their Rhodium Complexes

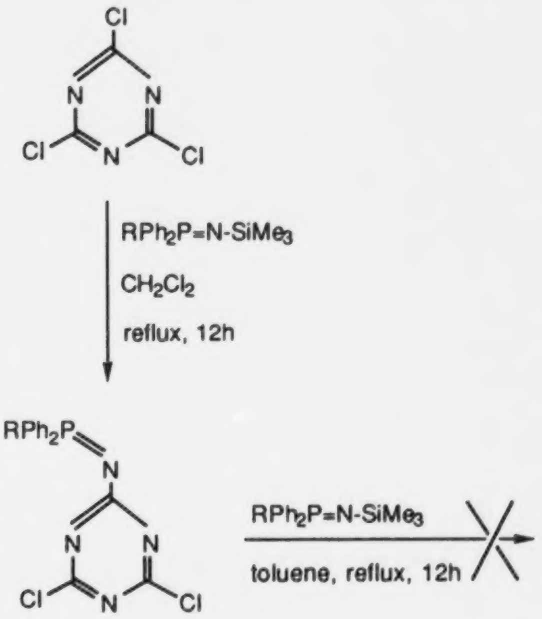
4.1. Phosphinimine Derivatives of Cyanuric Chloride, and Their Cationic Rh(I) Complexes

As discussed in Chapter 1, the chlorines in cyanuric chloride are very reactive and are easily substituted by nucleophilic reagents. Herein we describe a series of substitutions on the ring to form a series of multifunctional ligands. The azide route to prepare the mono, di or trisubstituted phosphinimine derivatives of cyanuric chloride as described in Chapter 1 is not desirable. An alternative route was devised, using $R_3P{=}N{-}SiMe_3$ as the reagent.

4.1.1. Synthesis and Properties of the Ligands

The reaction of cyanuric chloride with one equivalent of trimethylsilyl phosphinimine in refluxing CH_2Cl_2 gave the monosubstituted cyanuric derivatives (**6-1**)-(**6-3**) in good yields (Equation 4-1).

Equation 4-1:

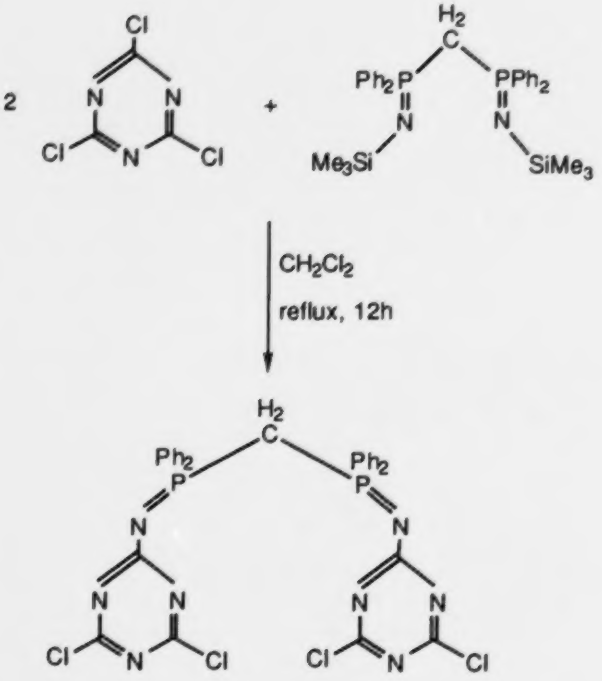

Cl
N
N
Cl
N
Cl
RPh$_2$P=N-SiMe$_3$
CH$_2$Cl$_2$
reflux, 12h
RPh$_2$P
N
N
N
Cl
N
Cl
RPh$_2$P=N-SiMe$_3$
toluene, reflux, 12h

6-1: R = Ph
6-2: R = Me
6-3: R = CH_2PPh_2

Further substitutions were not successful even when these reactions were carried out at a higher temperature (reflux in toluene for 12h).

The reaction of cyanuric chloride with one half equivalent of $Me_3SiN=P(Ph)_2CH_2P(Ph)_2=NSiMe_3$ in refluxing CH_2Cl_2 gave (**6-4**) (Equation 4-2).

Equation 4-2:



6-4

Compounds (**6-1**), (**6-2**) and (**6-4**) are colorless, air-stable but moisture sensitive solids which are soluble in most common organic solvents. The composition and structure of each of the compounds has been determined from the analytical data, mass spectra and ^{1}H and ^{31}P NMR spectroscopy. Molecular ions for each of the compounds are observed in the mass spectra. Phosphorus-31 NMR data are given in Table 4-1. The ^{31}P NMR spectra showed a single peak at 22.0, 23.5 and 16.6 ppm for the compounds (**6-1**), (**6-2**) and (**6-4**), respectively.

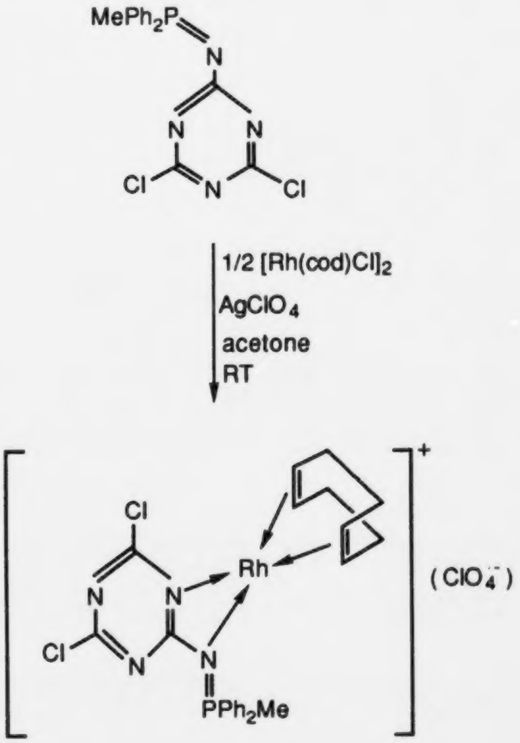
Compound (**6-3**) is a light yellow solid which is air-stable and soluble in most common organic solvents, but is very moisture sensitive. The molecular ion was observed in the mass spectrum. Phosphorus-31 NMR data are given in Table 4-1. The ^{31}P NMR spectrum showed two doublets at 24.7 ppm and -29.9 ppm respectively with

$^2J_{PP}$ = 59.8 Hz, consistent with the diphosphorus system. The elemental analysis data for (**6-3**) are not yet satisfactory and require further investigation.

4.1.2. Complexation Reaction of (6-1) with $[Rh(cod)Cl]_2$ and $AgClO_4$

To demonstrate the complexing ability of these ligands, we carried out the reaction of (**6-2**) with 1/2$[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25 °C and obtained complex (**6-5**) in high yield (Equation 4-3).

Equation 4-3:


MePh$_2$P
N
N
N
Cl
N
Cl
1/2 [Rh(cod)Cl]$_2$
AgClO$_4$
acetone
RT
Cl
N
N
Rh
Cl
N
N
PPh$_2$Me
+
(ClO$_4^-$)

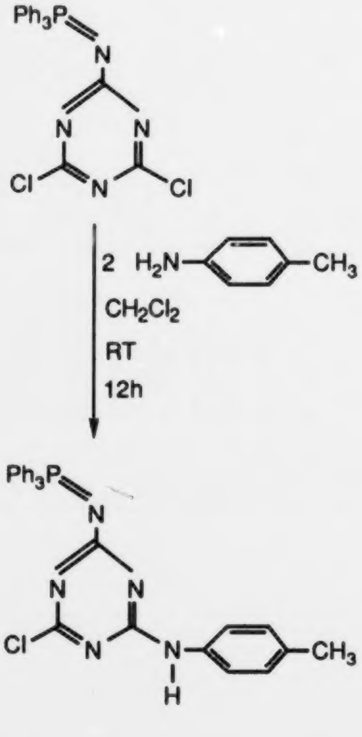
6-5

A peak corresponding to the molecular monocation of the complex was observed in the mass spectrum (FAB). The ^{31}P NMR spectrum of the complex showed a 21.2 ppm downfield shift compared with the ligand. The complex is light yellow. The solution molecular weight determination of the complex gave a value (498) that it is smaller than that of monomer (674) of the complex, probably because of dissociation of cation/anion pairs. The ligands thus show complexing abilities which can be further explored.

4.2. Mixed Phosphinimine Phenylamine Derivatives of Cyanuric Chloride

The reaction of (**6-1**) with two equivalents of *p*-methylphenylamine in CH_2Cl_2 at room temperature for 12h gave **6-6** in high yield. The role of the second equivalent of *p*-methylphenylamine is to trap the eliminated HCl (Equation 4-4).

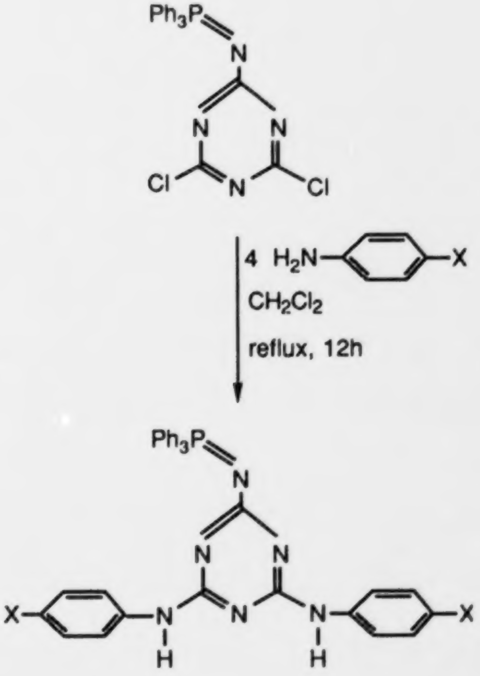
Equation 4-4:



6-6

The reaction of (**6-1**) with four equivalents of *para* substituted anilines in refluxing CH_2Cl_2 gave (**6-7**) and (**6-8**) in high yield and again excess of the aniline was used to trap the eliminated HCl (Equation 4-5). These reactions further illustrate that the chlorines in cyanuric chloride can be further substituted with appropriate reagents. Hence the inability of the silyliminophosphorane to act on the two remaining chlorines following the initial substitution as described above is probably not due to electronic deactivation of these two chlorine positions.

Equation 4-5:



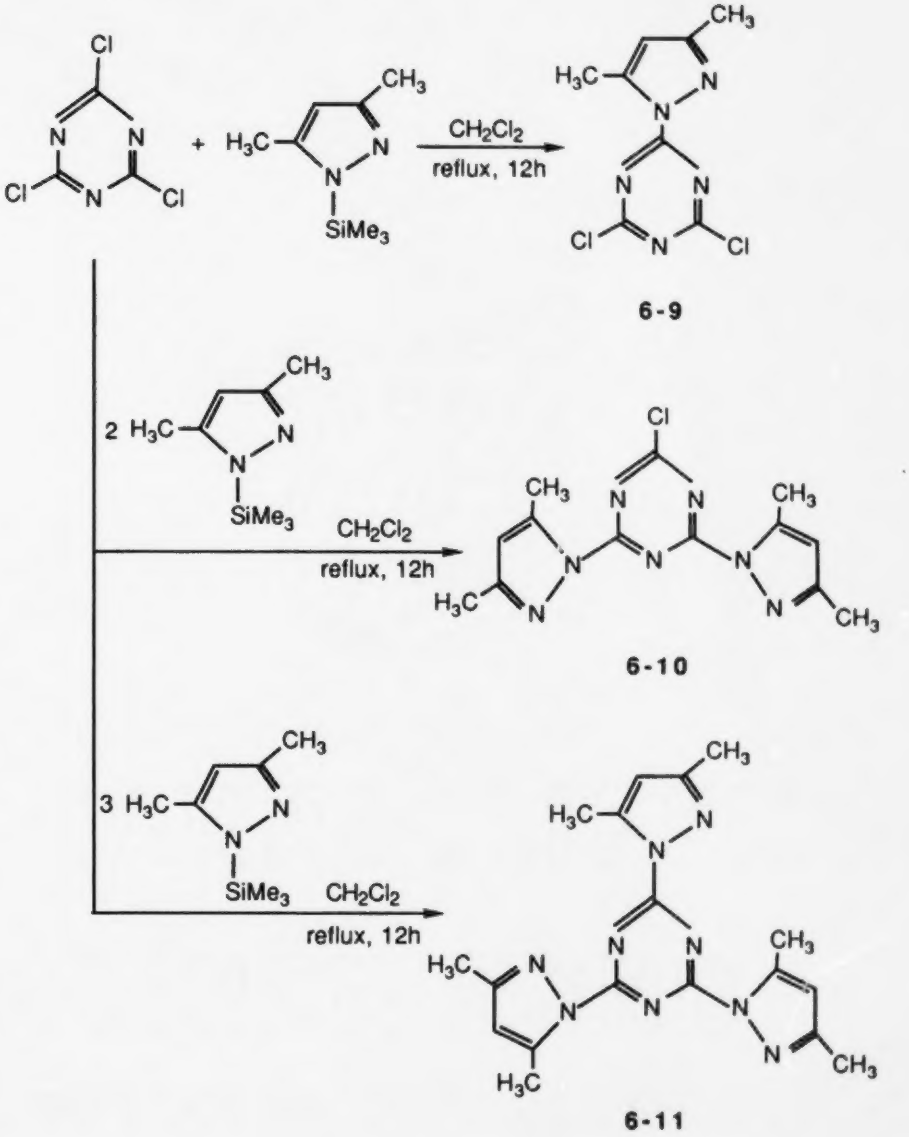
X = H, **6-7**

X = Me, **6-8**

Compounds (**6-6**) - (**6-8**) are air-stable solids which are soluble in most common organic solvents. Compounds (**6-6**) and (**6-7**) are colorless, but (**6-8**) is light yellow. The composition and structures of (**6-6**) - (**6-8**) have been determined from the analytical data, mass spectra and ^{1}H and ^{31}P NMR spectroscopy. Molecular ions for each of the compounds were observed in the mass spectra. Phosphorus-31 NMR data are given in Table 4-1. The ^{31}P NMR signals for (**6-6**) - (**6-8**) are 21.5, 21.6 and 21.5 ppm respectively which is an upfield shift of about 0.5 ppm compared with that of the precursor (**6-1**). Although (**6-6**) and (**6-8**) have the same chemical shift values, they are clearly distinct in other properties.

Reactions of cyanuric chloride with one, two or three equivalents of trimethylsilyl 3,5-dimethylpyrazole in refluxing CH_2Cl_2 gave mono-, di- or trisubstituted derivatives, (**6-9**) - (**6-11**) respectively (Equation 4-6).

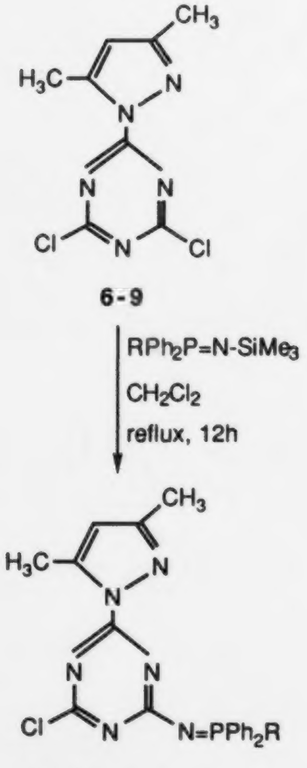
Equation 4-6:



Compounds **(6-9)** - **(6-11)** are colorless, air-stable but moisture sensitive solids which are soluble in most common organic solvents. Molecular ions for each of the compounds are observed in the mass spectra. Elemental analysis data are consistent with the formulae. Thus all three chlorines are readily replaced by this silylated reagent and so it is even more puzzling that there was no multiple substitution in the silylated imino phosphorane reactions described above.

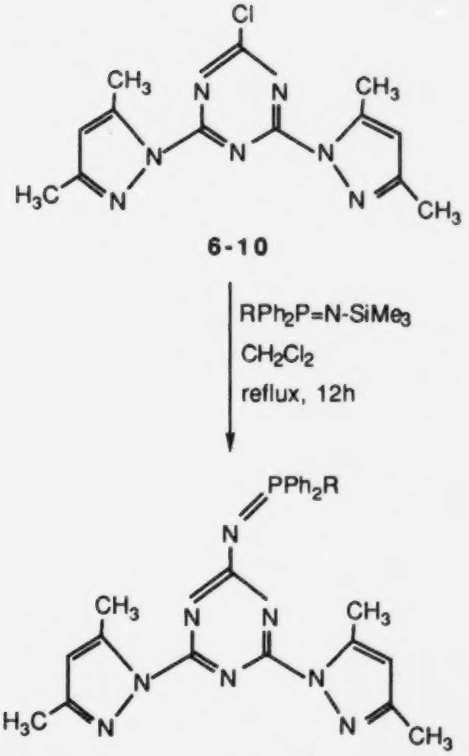
Compound (**6-9**), in which one chlorine atom is replaced by a pyrazole, reacts further with one equivalent of the trimethylsilyl phosphinimine or trimethylsilyl phosphoranophosphinimine to yield new ligands, (**6-12**) and (**6-13**). The bis pyrazole derivative (**6-10**) can also be further substituted by one phosphinimine to yield new ligands, (**6-14**) and (**6-15**), with heterocyclic and substituent imine functionalities. It is noteworthy that in the case of **6-13** and **6-15** there are free phosphine donor sites (Equation 4-7 and 4-8).

Equation 4-7:


CH$_3$
H$_3$C
N
N
N
N
Cl
N
Cl
6-9
RPh$_2$P=N-SiMe$_3$
CH$_2$Cl$_2$
reflux, 12h
CH$_3$
H$_3$C
N
N
N
N
Cl
N
N=PPh$_2$R

6 - 12: R = Ph
6 - 13: R = CH_2PPh_2

Equation 4-8:



6 -14: R = Ph
6 -15: R = CH_2PPh_2

Compounds (**6-12**) - (**6-15**) are colorless, air-stable but moisture sensitive solids which are soluble in most common organic solvents. Molecular ions for each of the compounds are observed in the mass spectra. Phosphorus-31 NMR data are given in Table 4-1. The ^{31}P NMR signals of (**6-12**) and (**6-14**) are single peaks at 35.7 ppm and 35.5 ppm respectively, which is a downfield shift of about 13.7 ppm and 13.5 ppm compared with that of (**6-1**). The ^{31}P NMR chemical shifts of (**6-13**) showed two doublets at 37.7 ppm and -28.7 ppm respectively, downfield shifts of about 13.0 ppm and 1.2 ppm compared with that of (**6-3**). The coupling constant between P^{III} and

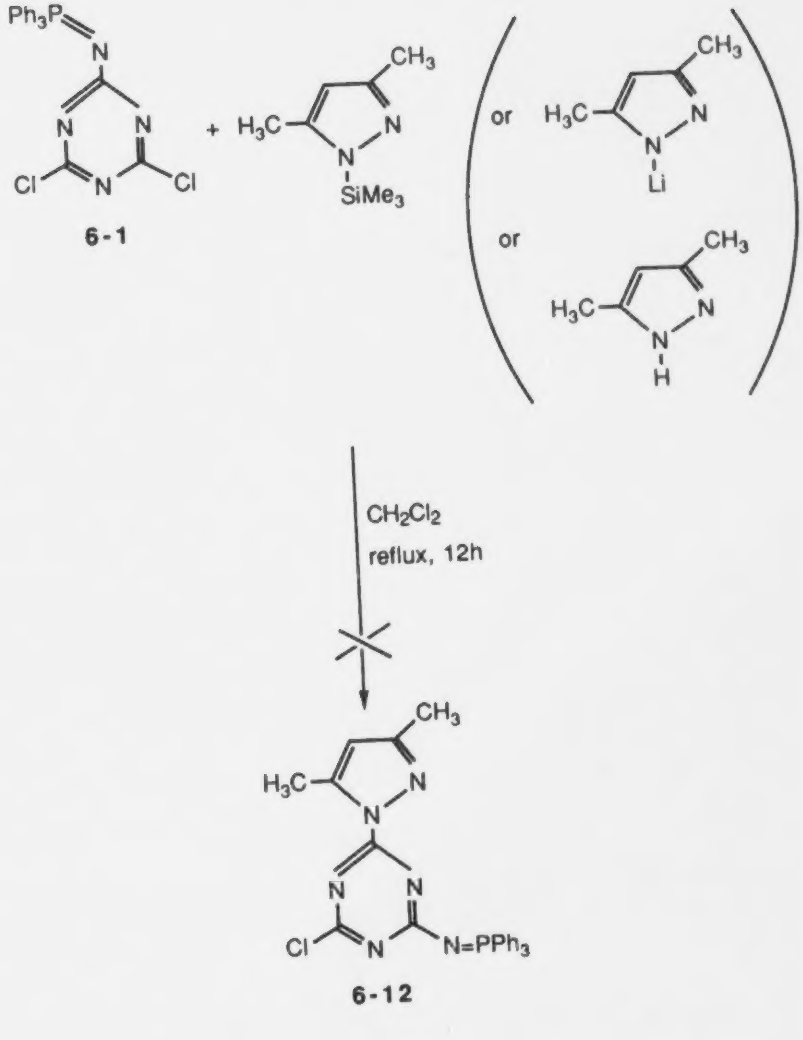
P^V is 62.8 Hz, which is 3 Hz larger than that of (**6-3**). The ^{31}P NMR spectrum of (**6-15**) showed two doublet signals at 37.2 ppm and -28.4 ppm respectively, a downfield shift of about 12.5 ppm and 1.5 ppm compared with that of (**6-3**). The coupling constant between P^{III} and P^V of (**6-15**) is 62.8 Hz which is again 3 Hz larger than that of (**6-3**).

The elemental analytical data for (**6-12**) and (**6-13**) are consistent with the proposed formulae, but satisfactory elemental analyses for (**6-14**) and (**6-15**) have not yet been achieved. There is no chlorine in the proposed formulae for (**6-14**) and (**6-15**), but the analyses show the presence of residual chlorine. Therefore, the materials are impure, and are admixtures with some of the starting materials. Considering that the full substitution of the third chlorine may need use of reaction at a higher temperature, a proposal for further work includes a repeat of the reactions in Equation 4-8, but using a higher boiling solvent such as THF or toluene.

Curiously, one cannot obtain (**6-12**) by reversing the sequence of substitution, that is first introducing the (Ph_3P=N-) group into cyanuric chloride, such as the preparation of (**6-1**) - (**6-3**), and then reacting the products with the trimethylsilyl-3,5-dimethylpyrazole (or lithium 3,5-dimethylpyrazole or 3,5-dimethylpyrazole) to complete the substitution (Equation 4-9). These subsequent substitutions do not proceed under conditions which are similar to those used throughout. Clearly, the phosphinimine deactivates the molecule to substitution of further halides, but the reason is not clear. Delocalization should not greatly affect the exocyclic chlorines in these positions.

Compound (**6-12**) cannot be accessed *via* the route described in Equation 4-9, but the two chlorines in (**6-1**) can be substituted readily by aniline. (Equation 4-4 and 4-5) This means that some unknown factors dominate this reaction.

Equation 4-9:

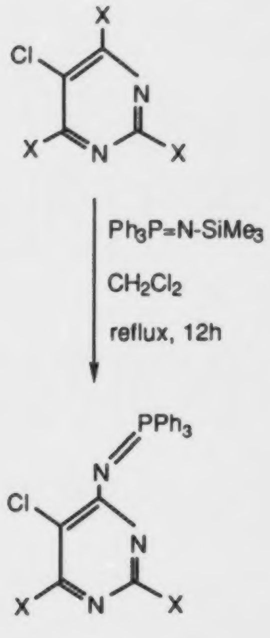

Ph3P=N
Cl
N
Cl
6-1
+
H3C
CH3
N
SiMe3
or
Li
or
H
CH2Cl2
reflux, 12h
N=PPh3
6-12

4.3. Phosphinimine Derivatives of a Halogenated Pyrimidine

In view of the unexpected deactivation of the cyanuric chloride with phosphinimines, we conducted a brief exploration of halogenated pyrimidines. Successful monosubstitution of this ring was observed in reactions analogous to those above.

Reactions of 5-chloro-2,4,6-trifluoro-pyrimidine or 2,4,5,6-tetrachloro-pyrimidine with $Ph_3P{=}N{-}SiMe_3$ gave monosubstituted pyrimidine derivatives (**6-16**) and (**6-17**) in high yield (Equation 4-10).

Equation 4-10:



X = F, 6-16
X = Cl, 6-17

Compounds (**6-16**) and (**6-17**) are colorless, air-stable, but moisture sensitive solids which are soluble in most common organic solvents. The molecular ions for (**6-16**) and (**6-17**) are observed in the mass spectra. For (**6-16**), the ^{31}P NMR spectrum showed a doublet at 18.14 ppm and the coupling constant is 3 Hz. The ^{19}F NMR spectrum of (**6-16**) showed two signals, one a single peak at -52.84 ppm and another a doublet at -69.42 ppm. The coupling constant is 3 Hz. Compared with those for the starting material, 5-chloro-2,4,6-trifluoropyrimidine, in which the ^{19}F NMR chemical shifts showed two signals at -52.8 and -69.4 ppm respectively with a 2:1 ratio, the ^{19}F NMR chemical shifts of (**6-16**) can be assigned. The signal at -69.42 ppm corresponds the fluorine between two nitrogens which coupled to the phosphorus, and the signal at -52.84 ppm corresponds to another fluorine. The elemental analysis data of (**6-16**) are consistent with the proposed formula. For (**6-17**), the ^{31}P NMR spectrum showed a single peak at 19.13 ppm.

Further substitution was not attempted, but would be of interest in view of the behavior of the cyanuric chloride system.

A preliminary study of metal complexation has been performed for (**6-16**) and (**6-17**), but the data have not yet given sufficient evidence about the nature of the product and the work is still in progress.

Table 4-1. ^{31}P NMR^{a} data for Compounds (**6-1**) - (**6-17**).

Compounds	**No.**	**δP** (ppm)
4,6-dichloro-2-(triphenylphosphinimino)-1,3,5-s-triazine	**6-1**	22.0(s)
4,6-dichloro-2-(methyldiphenylphosphinimino)-1,3,5-s-triazine	**6-2**	23.5(s)
4,6-dichloro-2-(N=PPh$_2$CH$_2$PPh$_2$)-1,3,5-s-triazine	**6-3**	24.7(d) -29.9(d) $^2J_{PP}$ = 59.8 Hz
Bis(diphenyl [3,5-dichloro-2,4,6-s-triazine]-imino-phosphino)methane	**6-4**	16.6(S)
[(4,6-dichloro-2-(methyldiphenylphosphinimino)-1,3,5-s-triazine) {N, N}Rh(cod)](ClO$_4$)	**6-5**	43.2(s)
4-chloro-6-(*p*-methylphenylamino)-2-(triphenylphosphinimino)-1,3,5-s-triazine	**6-6**	21.5
4,6-bis(phenylamino)-2-(triphenylphosphinimino)-1,3,5-s-triazine	**6-7**	21.6
4,6-bis(*p*-methylphenylamino)-2-(triphenylphosphinimino)-1,3,5-s-triazine	**6-8**	21.5
4,6-dichloro-2-(3,5-dimethylpyrazole)-1,3,5-s-triazine	**6-9**	---

Table 4-1. continued

Compounds	**No.**	δP (ppm)
6-chloro-2,4-bis(3,5-dimethylpyrazole)-1,3,5-s-triazine	**6-10**	---
2,4,6-tris(3,5-dimethylpyrazole)-1,3,5-s-triazine	**6-11**	---
6-chloro-4-(3,5-dimethylpyrazole)-2-(triphenylphosphinimino)-1,3,5-s-triazine	**6-12**	35.7
6-chloro-4-(3,5-dimethylpyrazole)-2-($N=PPh_2CH_2PPh_2$)-1,3,5-s-triazine	**6-13**	37.7(d) -28.7(d) $^2J_{PP}$ = 62.8 Hz
4,6-bis(3,5-dimethyl-pyrazole)-2-(triphenylphosphinimino)-1,3,5-s-triazine	**6-14**	35.5(s)
4,6-bis(3,5-dimethyl-pyrazole)-2-($N=PPh_2CH_2PPh_2$)-1,3,5-s-triazine	**6-15**	37.2(d) -28.4(d) $^2J_{PP}$ = 62.8 Hz
5-chloro-2,6-difluoro-4-(triphenylphosphinimino)-pyrimidine	**6-16**	18.1(d) $^5J_{PF}$ = 3 Hz
2,5,6-trichloro-4-(triphenylphosphinimino)-pyrimidine	**6-17**	19.1(s)

[a] Spectra obtained in $CDCl_3$ solution; ppm *vs* 85% H_3PO_4. Positive values indicate resonance to low field of the standard.

Chapter 5

Summary, Conclusions and Proposals for Future Work

Two new ligand systems have been created, each of which is based on fluoroaromatic phosphinimine ligands prepared by reactions of cyanofluorobenzenes with trimethylsilyl phosphinimines, and elimination of Me_3SiF. Active fluorine atoms at the 4 and 6 positions, each *para* to a CN group of 1,3-dicyanotetrafluorobenzene, can be substituted by phosphoranophosphinimine units to make mono or disubstituted fluoroaromatic compounds. The bifunctional phosphoranoimino phosphoranes, $Ph_2PCH_2P(Ph)_2{=}NAr$, are ligands which readily form chelated metal complexes.

In contrast to the multiple substitutions described above, reactions of 1,2- and 1,4-dicyanotetrafluorobenzene gave only monosubstituted derivatives, as previously described for related systems.[5] The reactions proceed smoothly and can be carried out sequentially. The multifunctional ligands readily react with $[Rh(CO)_2Cl]_2$ or $Pd(cod)Cl_2$ to form mono- and dinuclear complexes which exhibit either P-N chelate or P-P bidentate macrocyclic coordination. In the molecular structure of the dinuclear complex of Rh(I) with $[4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2\}_2]$, the two symmetrically P-N related chelates produce square planar geometry around each Rh(I), and the CO ligand *cis* to the phosphine. The whole molecule has C_2 symmetry with the two fluorine atoms lying on a twofold axis. The structures of the mononuclear P-P bidentate macrocyclic complexes of Rh(I) or Pd(II) have each been shown to be a bisphosphine chelate based on their complex second-order ^{31}P NMR spectra. The two P^{III} centers are *trans* coordinated to the metal center and the two N are not coordinated. The mixed Rh(I) and Pd(II) dimetallic complex of the ligand has also been obtained and characterized.

The second ligand system is derived from the same dicyanofluoroaromatic phosphinimine ligands, with monofunctional phosphinimine substituents. Cationic Rh(I) complexes of these ligands are formed in which coordination of the cyano substituent of the ring is involved. The nitrile groups and the imine nitrogen in the phosphinimine complexes coordinate to transition metals *via* either σ- or π-bonding modes. Similar π coordination by CN is also exhibited by unsubstituted *cis* dicyanofluoroaromatics. Both σ- and π-coordinated CN-Rh(I) complexes have been isolated and fully characterized. An EHMO calculation provides strong evidence that the lone pair of the nitrogen in the nitrile group is located in an anti-bonding orbital, which explains the observed increase in ν_{CN} on normal σ- bond coordination. Large decreases in ν_{CN} indicate a π-coordinated CN group. To date no crystals of suitable quality have been available for structural determinations. It is recommended that efforts be made to obtain crystals, for both σ- and π-coordinated CN-Rh(I) complexes. Further, the complexes show potential for catalytic utility which should be investigated.

In a complementary studies, phosphinimine *p*-benzoquinone derivatives and their cationic Rh(I) complexes have been synthesized and characterized. In parallel to the fluoroaromatics, reactions of tetrafluoro- or tetrachloro-*p*-benzoquinone with either one or two equivalents of trimethylsilyl phosphinimine were performed to create a series of mono- and disubstituted phosphinimine derivatives. The monosubstituted derivatives have been reacted with another equivalent of trimethylsilyl phosphinimine to form differently disubstituted derivatives. Both the mono- and disubstituted derivatives show very unusual ligating properties. The monosubstituted phosphinimine derivatives form σ-coordinated mononuclear Rh(I) complexes, and the disubstituted bis-phosphinimine derivatives form π-coordinated mononuclear Rh(I) complexes.

Reactions of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone with two equivalents of *p*-X-$C_6H_4NH_2$ gave a series of disubstituted *p*-benzoquinone derivatives. These ligands react with $[Rh(cod)Cl]_2$ and $AgClO_4$ to form a series of novel dinuclear complexes in which the nitrogen of the amine is bound to Rh by a covalent bond.

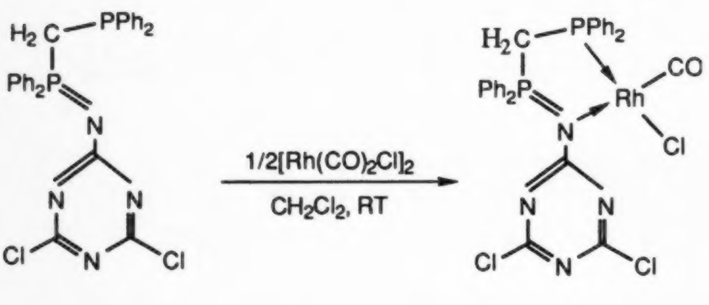
Reactions of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone with one equivalent of trimethylsilyl phosphinimine under mild conditions gave monosubstituted derivatives through elimination of Me_3SiCN. Two equivalents of trimethylsilyl phosphinimine gave the corresponding disubstituted derivatives. The monosubstituted derivatives also react with two equivalents of *p*-methylaniline to give a mixed disubstituted derivative. The monosubstituted derivative 3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone reacts with half mole equivalent of $[Rh(cod)Cl]_2$ and one equivalent of $AgClO_4$ to give a dimer in which the imine nitrogen and cyano nitrogen σ-coordinated to the Rh center. Reaction of phosphinimine-aniline mixed disubstituted derivative with Rh precursor only gives oxygen and imine nitrogen σ-coordinated mononuclear complex. The bis-phosphinimine disubstituted derivative reacts with Rh precursor to form π-coordinated mononuclear complexes. The parent quinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone reacts with Rh precursor to form cyano σ-coordinated dimer.

The electrochemical behavior of most of the benzoquinone derivatives has been investigated. In general, monosubstituted phosphinimine *p*-benzoquinone derivatives and mixed phosphinimine and aniline disubstituted *p*-benzoquinone derivatives reversibly accept two electrons. In contrast, the bis-phosphinimine disubstituted *p*-benzoquinone derivatives reversibly accept the first electron but addition of the second electron occurs irreversibly. Most of the Rh(I) complexes of quinone derivatives accept electrons irreversibly, giving clean electrochemical profiles.

These highly colored electrochemically active benzoquinone derivatives could be very useful as optical storage materials or in biological systems.[169] Future work should therefore explore applications of the molecules as dyes and pigments, and also the biological activities and the catalytic properties of various metal complexes which would be analogs of the Rh models synthesized herein. Since the coordination sites in the quinone phosphinimine derivatives are O and N which are hard base centers, future studies with the quinone derivatives should extend to the early transition-metal and high oxidation state (hard Lewis acid) centers. It is also recommended to keep trying to obtain crystals in order to fully characterize those quinone metal complexes.

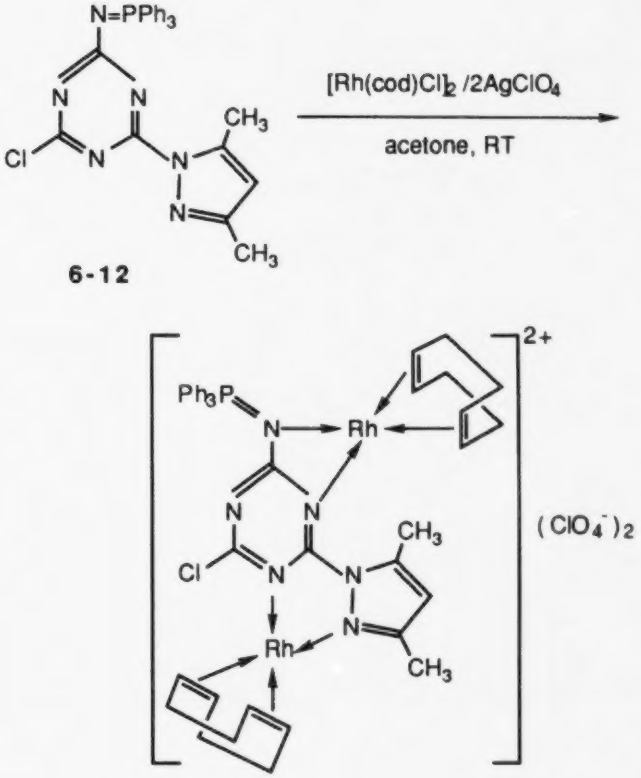
A third series of organic systems with phosphinimine substituents which has been created comprises derivatives of cyanuric chloride and chloro- or fluoropyrimidine. Preliminary studies have shown the potential of these systems as ligands. It is recommended that the coordination chemistry of these mixed hard(N)/soft(P) polydentate ligands be explored in depth. It is anticipated that mono- and polynuclear complexes will be synthesized, as shown in Equations 5-1, 5-2 and 5-3.

Equation 5-1:



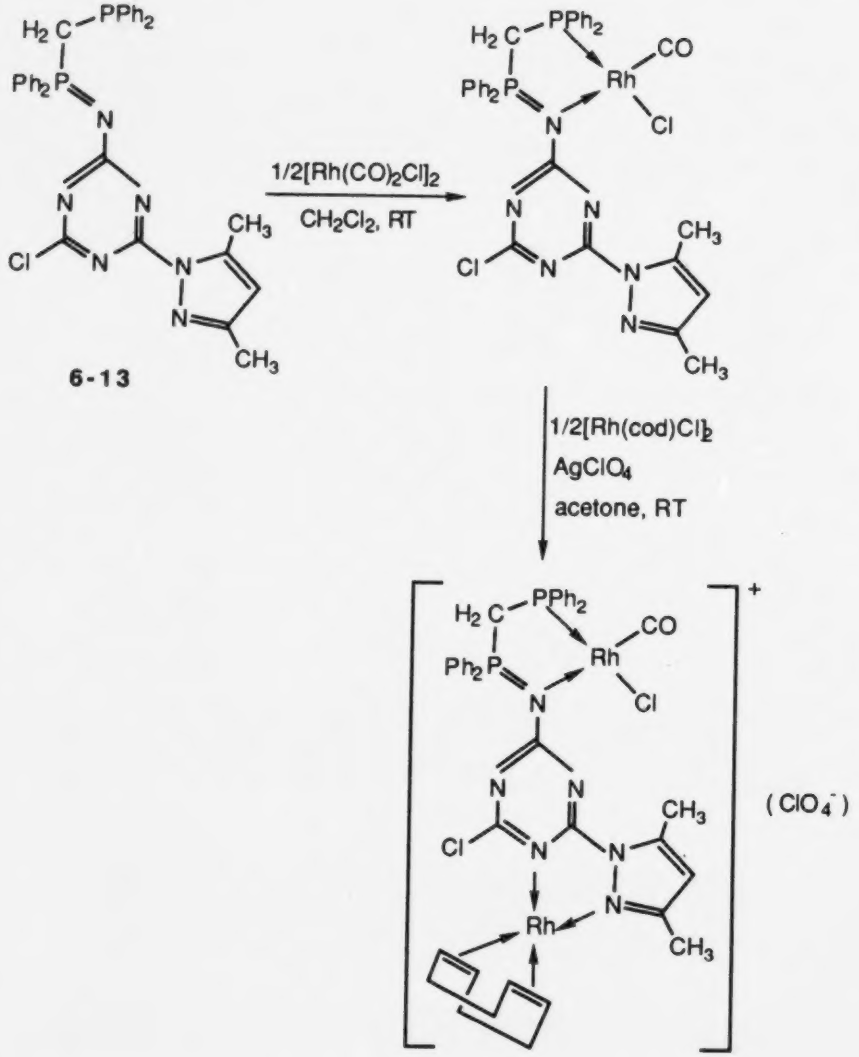
6-3

Equation 5-2:


N=PPh$_3$
N
N
Cl
N
CH$_3$
N
N
CH$_3$
[Rh(cod)Cl]$_2$ /2AgClO$_4$
acetone, RT
2+
Ph$_3$P
N
Rh
N
N
CH$_3$
Cl
N
N
N
Rh
CH$_3$
(ClO$_4^-$)$_2$

6-12

Equation 5-3:



6-13

H₂C—PPh₂
Ph₂P=N
N
N
Cl
N
N
CH₃
N
CH₃
1/2[Rh(CO)₂Cl]₂
CH₂Cl₂, RT
Rh
CO
Cl
1/2[Rh(cod)Cl]₂
AgClO₄
acetone, RT
+
(ClO₄⁻)

Chapter 6

Experimental

Experimental

All experimental manipulations were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried and distilled under argon prior to use: CH_2Cl_2, CH_3CN, THF and toluene were distilled from P_2O_5, P_2O_5/CaH_2, Na/benzophenone and Na respectively. The deuterated solvent, $CDCl_3$ was distilled and stored under argon before use. Commercial (Aldrich) supplies of dppm, Me_3SiN_3, 1,4-dicyanotetrafluorobenzene, 1,3-dicyanotetrafluorobenzene and 1,2-dicyanotetrafluorobenzene were used as obtained. $Ph_2PCH_2P(Ph)_2{=}NSiMe_3$ was prepared as previously described.[4]

Nuclear magnetic resonance spectra were recorded on Bruker WH-200 and Bruker WH-400 spectrometers using as the reference the deuterium signal of the solvent employed (respective operating frequencies: ^{1}H = 200.133 and 400.135 MHz, ^{13}C = 50.323 and 100.614 MHz, ^{31}P = 81.015 and 161.977 MHz, ^{19}F = 188.313 and 376.503 MHz). The ^{1}H chemical shifts are reported in ppm from external Me_4Si, the ^{31}P NMR spectra are reported in ppm from external 85% H_3PO_4, and the ^{19}F NMR spectra are reported in ppm from external $CFCl_3$. Positive values are shifts downfield. Low-resolution mass spectra (Electron Impact, EI) were recorded at 16 or 70 eV on an AEI MS50 spectrometer. Positive ion fast atom bombardment mass spectra (FAB-MS) were obtained by using Xe fast atoms on a customized AEI MS9 spectrometer.

Infrared spectra were recorded using a Nicolet 7199 infrared spectrometer. UV-visible spectra were recorded using a Hewlett Packard 8450A Diode Array Spectrophotometer. Elemental analyses were performed by the Microanalytical Services Laboratory at the University of Alberta. Melting points were ascertained by visual methods in unsealed capillaries. Osmometry measurements were made in CH_2Br_2 or *o*-dichlorobenzene solutions using a Corona Wescan Vapor Pressure Osmometer operated by the University of Alberta Microanalytical Services Laboratory. Crystal structure determinations were carried out by Dr. R. McDonald at the Structure Determination Lab, Department of Chemistry, University of Alberta and by Dr. A. A. Pinkerton and colleagues at the Department of Chemistry, University of Toledo.

Synthesis of 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}P(Ph)_2CH_2PPh_2)_2$ (1-1):

To a solution of $Me_3SiN{=}P(Ph)_2CH_2PPh_2$ (0.800 g; 1.70 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,3-dicyanotetrafluorobenzene (0.170 g; 0.85 mmol) also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain pure compound **1-1** (yield 0.32 g; 39%; cubic crystals, suitable for diffraction studies; mp: 292 °C). Anal. Calc'd for $C_{58}H_{44}N_4F_2P_2$: C, 72.65; H, 4.62; N, 5.84. MS (FAB, m/z): 959 (M+, 100%). Found: C, 72.37; H, 4.50; N, 5.85. ^1H NMR ($CDCl_3$): phenyl rings δ 7.05, 7.15, 7.30, 7.42, 7.75 (m, 40H); PCH_2P methylene δ 2.77 (dd, 2H, $^2J_{HP^V}$ = 12.40 Hz, $^2J_{HP^{III}}$ = 2.30 Hz).

Synthesis of 4,6-$(CN)_2C_6F_2$-1-$(N{=}P(Ph)_2CH_2P(Ph)_2)$-3-$(N{=}PPh_3)$ (1-2):

To a solution of $Me_3SiN{=}P(Ph)_2CH_2PPh_2$ (0.310 g; 0.66 mmol) in dry toluene (20 ml) was added dropwise a solution of 2,4-$(CN)_2C_6F_3N{=}PPh_3$ (0.300 g; 0.66 mmol), also in toluene (50 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a light yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain pure compound **1-2** (yield 0.52 g; 95%; cubic crystals, suitable for diffraction studies; mp: 231 °C). Anal. Calc'd for $C_{51}H_{37}N_4F_2P_3$: C, 73.20; H, 4.47; N, 6.70. MS (EI, m/z): 836 (M+, 100%). Found:

C, 72.67; H, 4.37; N, 6.74. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.10, 7.35, 7.55 (m, 35H), PCH_2P methylene δ 2.83(dd, 2H, $^2J_{HP^V}$ = 12.50 Hz, $^2J_{HP^{III}}$ = 2.30 Hz).

Synthesis of $4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}(N{=}PPh_2CH_2PPh_2)\text{-}3\text{-}(N{=}PPh_2Me)$ (1-3):

To a solution of $Me_3SiN{=}PPh_2CH_2PPh_2$ (0.300 g; 0.63 mmol) in dry toluene (20 ml) was added dropwise a solution of $2,4\text{-}(CN)_2C_6F_3N{=}PPh_2Me$ (0.250 g; 0.63 mmol), also in toluene (60 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a light yellow crystalline solid. This crude product was recrystallized from acetonitrile to obtain pure compound **1-3** (yield 0.35 g; 74%; colourless cubic crystals, suitable for diffraction studies; mp: 241 °C). Anal. Calc'd for $C_{46}H_{35}N_4F_2P_3$: C, 71.32; H, 4.55; N, 7.23. MS (EI, m/z): 775 (M+, 100 %). Found: C, 71.09; H, 4.56; N, 7.47. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.15, 7.28, 7.45, 7.70 (m, 20H), methyl group δ 1.63 (dd, 3H). PCH_2P methylene δ 2.91 (dd, 2H, $^2J_{HP}{}^{V}$ = 12.40 Hz, $^2J_{HP}{}^{III}$= 2.50 Hz).

Synthesis of

$4,6\text{-}(CN)_2C_6F_2\text{-}3\text{-}(N{=}PPh_3)\text{-}1\text{-}\{\overline{N{=}P(Ph)_2CH_2P(Ph)_2R}h(CO)Cl\}$

(1-4):

To a solution of $[Rh(CO)_2Cl]_2$ (30.0 mg; 0.077 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of $4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2\}\text{-}3\text{-}(N{=}PPh_3)$ (0.129g, 0.154 mmol), also in CH_2Cl_2 (20 ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was recrystallized from CH_2Cl_2/hexane (2:1) to obtain the pure compound **1-4**. (yield 0.134 g; 87%; mp: > 210 °C, decomp). Anal. Calc'd for $C_{52}H_{37}N_4OClF_2P_3Rh$: C, 62.26; H, 3.72; N, 5.58; Cl, 3.53. MS (FAB, m/z): 1003 (M+, 100 %). Found: C, 62.23; H, 3.65; N, 5.60; Cl, 3.96. ^{1}H NMR

($CDCl_3$): phenyl rings δ 7.25, 7.53, 7.68, 7.85 (m, 35H), PCH_2P methylene δ 2.91 (d, 2H, $^2J_{HP}$V = 12.00 Hz).

Synthesis of $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{\overline{N{=}P(Ph)_2CH_2P(Ph)_2Rh}(CO)Cl\}_2$ (1-5):

Method (A): To a solution of $[Rh(CO)_2Cl]_2$ (30.0 mg; 0.077 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{N{=}P(Ph)_2CH_2PPh_2\}_2$ (0.074 g; 0.077 mmol) also in CH_2Cl_2 (25ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid. This crude product was recrystallized from CH_2Cl_2/hexane (2:1) to obtain the dichloromethane solvate of **1-5**. (yield 64.0 mg; 60%; mp: 276-8 °C). Anal. Calc'd for $C_{61}H_{46}N_4O_2Cl_4F_2P_4Rh_2$: C, 53.22; H, 3.37; N, 4.07; Cl, 10.30. MS (FAB, m/z): 1255 ((M^+- Cl), 100 %); no parent peak (1292) was observed. Found: C, 53.11; H, 3.24; N, 4.06; Cl, 9.47. ^1H NMR ($CDCl_3$): phenyl rings δ 7.15, 7.30, 7.50, 7.80 (m, 40H), PCH_2P methylene δ 3.77 (m, 2H), δ 3.55 (m, 2H).

Method (B): In a 50 ml flask containing 10 ml CH_2Cl_2, compound (**1-6**) (see below) (0.037 g, 0.031 mmol) and $[Rh(CO)_2Cl]_2$ (0.001 g, 0.015 mmol) were mixed. The mixture was stirred at room temperature for 5h, after which the solvent was removed *in vacuo* to leave a yellow solid identified as (**1-5**) by ^{31}P, ^{19}F NMR and IR data.

Synthesis of $4,6\text{-(CN)}_2\text{C}_6\text{F}_2\text{-1,3-}\{\text{N=P(Ph)}_2\text{CH}_2\text{P(Ph)}_2\}_2\text{Rh(CO)Cl}$ (1-6):

Method (A): To a solution of $[\text{Rh(CO)}_2\text{Cl}]_2$ (30.0 mg; 0.077 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of $4,6\text{-(CN)}_2\text{C}_6\text{F}_2\text{-1,3-}\{\text{N=P(Ph)}_2\text{CH}_2\text{P(Ph)}_2\}_2$ (0.148 g; 0.15 mmol) also in CH_2Cl_2 (35 ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was recrystallized from CH_2Cl_2/hexane (2:1) to obtain **1-6** as a dichloromethane solvate. (yield 0.117 g; 63 %; mp: > 150 °C, decomp). Anal. Calc'd for $\text{C}_{60}\text{H}_{46}\text{N}_4\text{OCl}_3\text{F}_2\text{P}_4\text{Rh}$: C, 59.55; H, 3.83; N, 4.63; Cl, 8.79. MS (FAB, m/z): 1125 (M^+, 100%). Found: C, 59.55; H, 3.58; N, 4.69; Cl, 8.80. Molecular weight determination: 1041 (solvent: CH_2Br_2). ^{1}H NMR (CDCl_3): phenyl rings δ 7.30, 7.57 (m, 40H), PCH_2P methylene δ 3.38 (ddd, 2H), δ 5.35 (ddd, 2H).

Method (B): In a 50 ml flask containing 10 ml CH_2Cl_2, compound (**1-1**) (0.012 g, 0.013 mmol) and compound (**1-5**) (0.017 g, 0.013 mmol) were mixed. The mixture was stirred at room temperature for 5h, after which the solvent was removed *in vacuo* to leave a yellow solid which was identified as (**1-6**) by ^{31}P, ^{19}F NMR and IR data.

Synthesis of $4,6\text{-(CN)}_2\text{C}_6\text{F}_2\text{-1,3-}\{\overbracket{\text{N=P(Ph)}_2\text{CH}_2\text{P(Ph)}_2\text{P}}\text{dCl}_2\}_2$ (1-7):

To a solution of $[\text{Pd(cod)Cl}_2]$ (0.035g; 0.123 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of $4,6\text{-(CN)}_2\text{C}_6\text{F}_2\text{-1,3-}\{\text{N=P(Ph)}_2\text{CH}_2\text{PPh}_2\}_2$ (0.059 g; 0.062 mmol), also in CH_2Cl_2 (25ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was recrystallized from CH_2Cl_2/hexane (2:1) to obtain pure compound **1-7**. (yield 56.0 mg; 69%; mp: > 200 °C, decomp.). Anal. Calc'd for $C_{58}H_{44}N_4Cl_4F_2P_4Pd_2$: C, 53.04; H, 3.38; N, 4.27; Cl, 10.80. MS (FAB, m/z): 1279 ((M^+- Cl)). Found: C, 53.06; H, 3.35; N, 3.98; Cl, 10.86. ^1H NMR ($CDCl_3$): phenyl rings δ 7.15, 7.25, 7.50, 7.75 (m, 40H), PCH_2P methylene δ 3.90 (m, 2H), δ 3.50 (m, 2H).

Synthesis of $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2\}_2PdCl_2$ (1-8):

To a solution of [Pd(cod)Cl_2] (60.0 mg; 0.209 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2\}_2$ (0.200 g; 0.209 mmol), also in CH_2Cl_2 (35 ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was recrystallized from CH_2Cl_2/pentane to obtain the 1:1 pentane solvate of **1-8**. (yield 0.190 g; 75 %; mp: > 140 °C, decomp). Anal. Calc'd for $C_{63}H_{56}N_4Cl_2F_2P_4Pd$: C, 62.62; H, 4.67; N, 4.64; Cl, 5.87. MS (FAB, m/z): 1101 (M^+-Cl). Found: C, 62.63; H, 3.81; N, 4.95; Cl, 5.91. ^1H NMR ($CDCl_3$): phenyl rings δ 7.20, 7.45, 7.55 (m, 40H), PCH_2P methylene δ 4.20 (broad, 4H).

Synthesis of

$4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2Rh(CO)Cl\}\text{-}3\text{-}$
$\{N{=}P(Ph)_2CH_2P(Ph)_2PdCl_2\}$ (1-9):

Method (A): To a solution of [Pd(cod)Cl_2] (0.014g; 0.049 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}\{N{=}P(Ph)_2CH_2P(Ph)_2\}_2Rh(CO)Cl$ (0.055 g; 0.049 mmol), also in CH_2Cl_2 (35 ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was recrystallized from

CH_2Cl_2/pentane to obtain pure compound **1-9**. (yield 0.050 g; 78%; mp: > 200 °C, decomp). Anal. Calc'd for $C_{59}H_{44}N_4Cl_3F_2P_4RhPd$: C, 54.40; H, 3.40; N, 4.30; Cl, 8.17. MS (FAB, m/z): 1267 (M^+-Cl). Found: C, 54.94; H, 3.37; N, 4.22; Cl, 8.38. ^1H NMR ($CDCl_3$): phenyl rings δ 7.20, 7.45, 7.75 (m, 40H), PCH_2P methylene δ 3.65, 3.70, 3.90 (m, 4H).

Method (B): To a solution of $[Rh(CO)_2Cl]_2$ (0.013 g; 0.033 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise a solution of 4,6-$(CN)_2C_6F_2$-1,3-$\{N{=}P(Ph)_2CH_2P(Ph)_2\}_2PdCl_2$ (**1-8**) (0.076 g; 0.066 mmol) also in CH_2Cl_2 (35 ml). The reaction mixture was stirred at room temperature for 4h before the solvent was removed *in vacuo* to leave a yellow solid which was identified as (**1-9**) by ^{31}P NMR.

Synthesis of 4,6-$(CN)_2C_6F_2$-1,3-$(N{=}PPh_3)_2$ (2-1):

To a solution of $Me_3SiN{=}PPh_3$ (0.699 g; 2.00 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,3-dicyanotetraflurobenzene (0.200 g; 1.00 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-1** (yield 0.61g; 85%; cubic crystals, suitable for diffraction studies; mp: 329 °C). Anal. Calc'd for $C_{44}H_{30}N_4F_2P_2$: C, 73.95; H, 4.23; N, 7.84. MS(EI, m/z): 714 (M+, 100%). Found: C, 73.37; H, 4.04; N, 7.73. ^{19}F NMR ($CDCl_3$): δ (F_2 (adjacent to CN)) -107.4 ppm (a doublet of triplets, 1F, $^5J_{F_1F_2}$ = 11Hz, $^5J_{PF_2}$ = 4.5 Hz). δ (F_1) -135.3 ppm (a doublet of triplets, 1F, $^5J_{F_1F_2}$ = 11Hz, $^4J_{PF_1}$ = 10.8 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.50 ppm (m, 30H).

Synthesis of $4,6\text{-}(CN)_2C_6F_2\text{-}1,3\text{-}(N{=}PPh_2Me)_2$ (2-2):

To a solution of $Me_3SiN{=}PPh_2Me$ (1.437 g; 5.00 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,3-dicyanotetraflurobenzene (0.500 g; 2.50 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-2** (yield 1.32 g; 89%; cubic crystals, suitable for diffraction studies; mp: 270 °C). Anal. Calc'd for $C_{34}H_{26}N_4F_2P_2$: C, 69.15; H, 4.44; N, 9.49. MS (EI, m/z): 590 (M+, 100 %). Found: C, 68.33; H, 4.48; N, 9.60. ^{19}F NMR ($CDCl_3$): δ (F_2 (adjacent to CN)) -107.1 (a doublet of triplets, 1F, $^5J_{F_1F_2}$ = 11Hz, $^5J_{PF_2}$ = 4.6 Hz). δ (F_1) -142.3 (a doublet of triplets, 1F, $^5J_{F_1F_2}$ = 11Hz, $^4J_{PF_1}$ = 13.5 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.45, 7.70 ppm (m, 20H); two methyl groups δ 1.80 ppm (d, 6H, J=13 Hz).

Synthesis of $4,6\text{-}(CN)_2C_6F_2\text{-}1\text{-}(N{=}PPh_3)\text{-}3\text{-}(N{=}PPh_2Me)$ (2-3):

To a solution of $Me_3SiN{=}PPh_2Me$ (0.200 g; 0.70 mmol) in dry toluene (20 ml) was added dropwise a solution of $2,4\text{-}(CN)_2C_6F_3N{=}PPh_3$ (0.279 g; 0.61 mmol), also in toluene (50 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a light yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-3** (yield 0.31 g; 78%; cubic crystals, suitable for diffraction studies; mp: 264 °C). Anal. Calc'd for $C_{39}H_{28}N_4F_2P_2$: C, 71.78; H, 4.32; N, 8.58. MS (EI, m/z): 652 (M+, 100 %). Found: C, 71.52; H, 4.26; N, 8.57. ^{19}F NMR ($CDCl_3$): δ (F_2 (adjacent to CN)) -107.3 ppm (ddd, 1F, $^5J_{F_1F_2}$ = 11.3 Hz, $^5J_{P_1F_2}$ = 4.5 Hz, $^5J_{P_2F_2}$ = 4.7 Hz). δ (F_1) -139.0 ppm (ddd, 1F, $^5J_{F_1F_2}$ = 11Hz, $^4J_{P_1F_1}$ = 10.7 Hz, $^4J_{P_2F_1}$ = 13.8 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.5 ppm (m, 20H), methyl group δ 1.7 ppm (dd, 3H).

Synthesis of 2,4-$(CN)_2C_6F_3$-1-($N=PPh_3$) (2-4):

To a solution of $Me_3SiN=PPh_3$ (0.874 g; 2.50 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,3-dicyanotetraflurobenzene (0.500 g; 2.50 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-4** (yield 1.00 g; 88%; mp: 228 °C). Anal. Calc'd for $C_{26}H_{15}N_3F_3P$: C, 68.28; H, 3.31; N, 9.19. MS (EI, m/z): 457 (M+, 100 %). Found: C, 68.22; H, 3.15; N, 9.23. ^{19}F NMR ($CDCl_3$): δ (F_3 (between two CN)) -104.80 ppm (a doublet of doublets, 1F, $^5J_{F_1F_3} = 11.3$ Hz, $^5J_{PF_3} = 4.0$ Hz). δ (F_1 (close to P)) -150.64 ppm (ddd, 1F, $^3J_{F_1F_2} = 22.6$ Hz, $^5J_{F_1F_3} = 11.3$ Hz, $^4J_{PF_1} = 7.9$ Hz). δ (F_2) -125.78 ppm (a doublet, 1F, $^3J_{F1F2} =$ 22.6 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.75 ppm (m, 15H).

Synthesis of 2,4-$(CN)_2C_6F_3$-1-($N=PPh_2Me$) (2-5):

To a solution of $Me_3SiN=PPh_2Me$ (0.600 g; 2.09 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,3-dicyanotetraflurobenzene (0.418 g; 2.09 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-5** (yield 0.67 g; 81%; mp: 176 °C). Anal. Calc'd for $C_{21}H_{13}N_3F_3P$: C, 63.80; H, 3.31; N, 10.63. MS(EI, m/z): 395 (M+, 100%). Found: C, 64.30; H, 3.27; N, 10.30. ^{19}F NMR ($CDCl_3$): δ (F_3 (between two CN)) -104.75 ppm (a doublet of doublets, 1F, $^5J_{F_1F_3} = 7.5$ Hz, $^5J_{PF_3} = 4.2$ Hz). δ (F_1 (close to P)) -153.67 ppm (ddd, 1F, $^3J_{F_1F_2} = 22.6$ Hz, $^5J_{F_1F_3} = 7.5$ Hz, $^4J_{PF_1} = 9.9$ Hz). δ (F_2) -126.15 ppm (a doublet, 1F, $^3J_{F_1F_2} =$ 22.6 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.85 ppm (m, 10H), methyl group δ 2.30 ppm (dd, 3H).

Synthesis of 3,4-$(CN)_2C_6F_3$-1-(N=PPh_3) (2-6):

To a solution of $Me_3SiN{=}PPh_3$ (0.350 g; 1.00 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,2-$(CN)_2C_6F_4$ (0.200 g; 1.00 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-6** (yield 0.42 g; 92%; mp: 196 °C). Anal. Calc'd for $C_{26}H_{15}N_3F_3P$: C, 68.28; H, 3.31; N, 9.19. MS (EI, m/z): 457 (M+, 100 %). Found: C, 67.84; H, 3.24; N, 9.27. ^{19}F NMR ($CDCl_3$): δ (F_1 (para to one CN)) -137.0 ppm (ddd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^4J_{F_1F_2}$ = 22.6 Hz, $^3J_{PF_1}$ = 4.0 Hz). δ (F_2 (close to P and para to F_3)) -116.0 ppm (ddd, 1F, $^4J_{F_1F_2}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz, $^3J_{PF_2}$ = 7.0 Hz), δ F_3 -146.0 ppm (dd, 1F, $^3J_{F_1F_3}$= 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.60 ppm (m, 15H).

Synthesis of 3,4-$(CN)_2C_6F_3$-1-(N=PPh_2Me) (2-7):

To a solution of $Me_3SiN{=}PPh_2Me$ (0.700 g; 2.44 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,2-$(CN)_2C_6F_4$ (0.487 g; 2.44 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave an orange yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-7** (yield 0.54 g; 56%; mp: 160 °C). Anal. Calc'd for $C_{21}H_{13}N_3F_3P$: C, 63.80; H, 3.31; N, 10.63. MS (EI, m/z): 395 (M+, 100 %). Found: C, 63.93; H, 3.30; N, 10.63. ^{19}F NMR ($CDCl_3$): δ (F_1 (para to one CN)) -139.0 ppm (ddd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^4J_{F_1F_2}$ = 22.6 Hz, $^3J_{PF_1}$ = 4.0 Hz). δ (F_2 (close to P and para to F_3)) -117.8 ppm (ddd, 1F, $^4J_{F_1F_2}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz, $^3J_{PF_2}$ = 7.0 Hz), δ F_3 -32.8 ppm (dd, 1F, $^3J_{F_1F_3}$ = 22.6 Hz, $^5J_{F_2F_3}$ = 7.5 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.75 ppm (m, 10H), methyl group δ 2.25 ppm (d, 3H).

Synthesis of 2,5-$(CN)_2C_6F_3$-1-($N=PPh_3$) (2-8):

To a solution of $Me_3SiN=PPh_3$ (0.250 g; 0.715 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,4-$(CN)_2C_6F_4$ (0.143 g; 0.715 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-8** (yield 0.28 g; 86%; mp: 181 °C). Anal. Calc'd for $C_{26}H_{15}N_3F_3P$: C, 68.28; H, 3.31; N, 9.19. MS (EI, m/z): 457 (M+, 100 %). Found: C, 68.07; H, 3.12; N, 9.06. ^{19}F NMR ($CDCl_3$): δ (F_1 (close to P)) -118.1 ppm (ddd, 1F, $^5J_{F_1F_2}$ = 13 Hz, $^4J_{F_1F_3}$ = 8 Hz, $^4J_{PF_1}$ = 7.0 Hz). δ (F_2 (para to P)) -133.7 ppm (ddd, 1F, $^3J_{F_2F_3}$ = 21 Hz, $^4J_{F_1F_2}$ = 13 Hz, $^6J_{PF_2}$ = 3.0 Hz), δ F_3 -146.0 ppm (dd, 1F, $^3J_{F_2F_3}$ = 21 Hz, $^5J_{F_1F_3}$ = 8 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.55, 7.75 ppm (m, 15H).

Synthesis of 2,5-$(CN)_2C_6F_3$-1-($N=PPh_2Me$) (2-9):

To a solution of $Me_3SiN=PPh_2Me$ (0.300 g; 1.04 mmol) in dry toluene (20 ml) was added dropwise a solution of 1,4-$(CN)_2C_6F_4$ (0.200 g; 1.00 mmol), also in toluene (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave an orange yellow crystalline solid. The crude product was recrystallized from acetonitrile to obtain pure compound **2-9** (yield 0.22 g; 56%; mp: 125 °C). Anal. Calc'd for $C_{21}H_{13}N_3F_3P$: C, 63.80; H, 3.31; N, 10.63. MS (EI, m/z): 395 (M+, 100%). Found: C, 64.02; H, 3.22; N, 10.63. ^{19}F NMR ($CDCl_3$): δ (F_1 (close to P)) -121.5 ppm (ddd, 1F, $^5J_{F_1F_3}$ = 11.3 Hz, $^4J_{F_1F_2}$ = 7.5 Hz, $^4J_{PF_1}$ = 9.4 Hz). $^3J_{F_2F_3}$ = 22.6 Hz, δ (F_2 (para to P)) -133.7 ppm (ddd, 1F, $^3J_{F_2F_3}$ = 22.6 Hz, $^4J_{F_1F_2}$ = 7.5 Hz, $^6J_{PF_2}$ = 3.9 Hz), δ F_3 -146.5 ppm (dd, 1F, $^3J_{F_2F_3}$ = 22.6 Hz, $^5J_{F_1F_3}$ = 11.3 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.25, 7.55, 7.80 ppm (m, 10H), methyl group δ 2.25 ppm (dd, 3H).

Synthesis of [5-(CN)-C_6F_3-2-(π-CN)-1-(N=PPh_3)Rh(cod)](ClO_4) (2-10):

To a 100 ml flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.200 mmol) and 15 ml acetone. The solution was stirred for 15 mins and then the solution was filtered and transferred to a flask in which contained 2,5-$(CN)_2C_6F_3$-1-(N=PPh_3) (0.092 g; 0.200 mmol) in 15 ml acetone. The resultant yellow solution was stirred at room temperature for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain the one sixth dichloromethane solvate of **2-10**. (yield 0.10 g; 64%; mp: > 165 °C decomp). Anal. Calc'd for $C_{34}H_{27}N_3F_3PRhClO_4 \cdot 1/6CH_2Cl_2$: C, 52.47; H, 3.52; N, 5.37; Cl, 6.04. MS (FAB): 668 (monocation). Found: C, 52.38; H, 3.53; N, 5.11; Cl, 6.01. ^{19}F NMR (CD_2Cl_2): (F ortho, meta, or para relative to the imino substituent): $\delta(F_o)$ -116.8 ppm (singlet, 1F), $\delta(F_p)$ -133.6 ppm (singlet, 1F), $\delta(F_m)$ -146.7 ppm (singlet, 1F). ^1H NMR (CD_2Cl_2): phenyl rings, δ 7.7 ppm (m, 15H); cod group: δ 4.5 ppm (broad, 4H, HC=), δ 2.55 ppm (broad, 4H, H_2C), δ 1.95 ppm (broad, 4H, H_2C). Molecular weight determination: 590 (solvent: CH_2Br_2).

Synthesis of [5-(CN)-C_6F_3-2-(π-CN)-1-(N=PPh_2Me)Rh(cod)](ClO_4) (2-11):

To a 100 ml flask were added $[Rh(cod)Cl]_2$ (0.022 g; 0.044 mmol), $AgClO_4$ (0.018 g; 0.089 mmol) and 15 ml acetone. The solution was stirred for 15 mins and then the solution was filtered and transferred to a flask in which contained 2,5-$(CN)_2C_6F_3$-1-(N=PPh_2Me) (0.035 g; 0.089 mmol) in 15 ml acetone. The resultant yellow solution was stirred at room temperature for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain pure compound **2-11**. (yield 0.04 g; 64%; mp: >

150 °C decomp). Anal. Calc'd for $C_{29}H_{25}N_3F_3PRhClO_4$: C, 49.35; H, 3.57; N, 5.95; Cl, 5.02. MS (FAB): 606 (monocation). Found: C, 49.47; H, 3.55; N, 5.60; Cl, 5.06. ^{19}F NMR (CD_2Cl_2): (F ortho, meta, or para relative to the imino substituent): $\delta(F_o)$ -118.9 ppm (singlet, 1F), $\delta(F_p)$ -132.6 ppm (singlet, 1F), $\delta(F_m)$ -146.2 ppm (singlet, 1F). ^1H NMR (CD_2Cl_2): phenyl rings, δ 7.6, 7.8 ppm (m, 10H); cod group: δ 4.50 ppm (broad, 4H, HC=), δ 2.50 ppm (broad, 4H, H_2C), δ 1.95 ppm (broad, 4H, H_2C); methyl group: 2.30 ppm (d, 3H, $^2J_{P\text{-}H}$ = 13 Hz). Molecular weight determination: 654 (solvent: CH_2Br_2).

Synthesis of [4-(CN)-C_6F_3-2-(π-CN)-1-(N=PPh_2Me)Rh(cod)](ClO_4) **(2-12):**

To a 100 ml flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.200 mmol) and 15 ml acetone. The solution was stirred for 15 mins and then the solution was filtered and transferred to a flask in which contained 2,4-$(CN)_2C_6F_3$-1-(N=PPh_2Me) (0.079g; 0.200 mmol) in 15 ml acetone. The resultant yellow solution was stirred at RT for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain pure compound **2-12**. (yield 0.075g; 53%; mp: 204-206 °C). Anal. Calc'd for $C_{29}H_{25}N_3F_3PRhClO_4$: C, 49.35; H, 3.57; N, 5.95; Cl, 5.02. MS(FAB): 606 ([LRh(cod)]). Found: C, 49.49; H, 3.34; N, 5.72; Cl, 5.39. ^{19}F NMR (CD_2Cl_2): $\delta(F_3$(between two CN))-100.4 ppm (s, 1F), $\delta(F_1$(close to P) -152.1 ppm (broad, 1F), $\delta(F_2)$ -123.8 ppm (d, J = 20 Hz, 2F); ^1H NMR (CD_2Cl_2): phenyl rings, δ 7.55, 7.60, 7.75 ppm (m, 10H); Methyl group, δ 2.35 ppm (d, $^2J_{P\text{-}H}$ = 12 Hz); cod group: δ 4.55 ppm (s, 4H, HC=), δ 2.50 ppm (broad doublet, 4H, H_2C-), δ1.95 ppm (broad, 4H, H_2C-). Molecular weight determination: not desolved in the required solvents.

Synthesis of $[(\mathrm{cod})\overline{\mathrm{Rh\text{-}1\text{-}(MePh_2P{=}N}}\mathrm{\text{-})C_6F_2\text{-}2\text{-}CN\text{-}5\text{-}(N{=}PPh_2Me)\text{-}4\text{-}(CN)Rh(cod)}]_n(\mathrm{ClO_4})_{2n}$ (2-13):

To a 100 ml flask were added $[\mathrm{Rh(cod)Cl}]_2$ (0.049 g; 0.100 mmol), $\mathrm{AgClO_4}$ (0.042 g; 0.200 mmol) and 15 ml acetone. The solution was stirred for 15 mins and then the solution was filtered and transferred to a flask in which contained 4,6-$(\mathrm{CN})_2\mathrm{C_6F_2}$-1,3-$(\mathrm{N{=}PPh_2Me})_2$ (0.059 g; 0.100 mmol) in 15 ml acetone. The resultant yellow solution was stirred at room temperature for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain pure compound **2-13**. (yield 0.08g; 66%; mp: > 170 °C decomp). Anal. Calc'd for $\mathrm{C_{50}H_{50}N_4F_2P_2Rh_2(ClO_4)_2}$: C, 49.57; H, 4.14; N, 4.62; Cl, 5.85. MS(FAB): 801([LRh(cod)]), 903 ([RhLRh(cod)]), 1012 ($[\mathrm{LRh_2(cod)_2}]$), 1283 ($[\mathrm{L_2Rh}]$) and 1391 ([L2Rh(cod)]). Found: C, 50.11; H, 4.26; N, 4.51; Cl, 5.83. ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ($\mathrm{F_1}$(between two imines)) -143.2 ppm (broad, 1F), δ($\mathrm{F_2}$) -102.06 ppm (broad, 1F). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): phenyl rings, δ 7.50 ppm (m, 20H). Methyl group, δ 1.90 ppm (broad, 6H); cod group: δ 4.45 ppm (broad, 8H, HC=), δ 2.55 ppm (broad, 8H, $\mathrm{H_2C}$-), δ1.95 ppm (broad, 8H, $\mathrm{H_2C}$-).

Synthesis of $\{(3{,}4\text{-}(\mathrm{CN})_2\mathrm{C_6F_3}\text{-}1\text{-}(\mathrm{N{=}PPh_3})\mathrm{Rh(cod)})_2\}(\mathrm{ClO_4})_2$ (2-14):

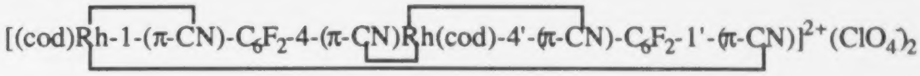
To a 100 ml flask were added $[\mathrm{Rh(cod)Cl}]_2$ (0.049 g; 0.100 mmol), $\mathrm{AgClO_4}$ (0.042 g; 0.20mmol) and 15 ml acetone. The resulting solution was stirred for 15 mins and then filtered and transferred to a flask containing 3,4-$(\mathrm{CN})_2\mathrm{C_6F_3}$-1-$(\mathrm{N{=}PPh_3})$ (0.092 g; 0.200 mmol) in 15 ml acetone. The resultant yellow solution was stirred at room temperature for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain pure compound **2-14**. (yield 0.085g; 55%; mp: > 140 °C decomp). Anal. Calc'd for $C_{68}H_{54}N_6F_6P_2Rh_2Cl_2O_8$: C, 53.18; H, 3.54; N, 5.47; Cl, 4.62. MS(FAB): 668(monocation). Found: C, 53.11; H, 3.48; N, 5.14; Cl, 5.08. ^{19}F NMR ($CDCl_3$): $\delta(F_1$(between imine and F_3))-135.0 ppm (broad, 2F), $\delta(F_2$(between imine and one CN) -113.1 ppm (broad doublet, J = 21 Hz, 2F), $\delta(F_3$(between F_1 and one CN)) -129.9 ppm (broad doublet, J = 21 Hz, 2F); ^1H NMR (CD_2Cl_2): phenyl rings, δ 7.45, 7.55 ppm (m, 30H); δ 4.5 ppm (s, 8H, HC=), δ 2.45 ppm (broad, 8H, H_2C), δ 1.90 ppm (broad, 8H, H_2C-). Molecular weight determination: 918 (solvent: CH_2Br_2).

Synthesis of {(3,4-$(CN)_2C_6F_3$-1-(N=PPh_2Me)Rh(cod))$_2$}$(ClO_4)_2$ (2-15):

To a 100 ml flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.20mmol) and 15 ml acetone. The solution was stirred for 15 mins and then the solution was filtered and transferred to a flask in which contained 3,4-$(CN)_2C_6F_3$-1-(N=PPh_2Me) (0.079 g; 0.200 mmol) in 15 ml acetone. The resultant yellow solution was stirred at room temperature for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain pure compound **2-15**. (yield 0.10 g; 81%; mp: > 150 °C decomp). Anal. Calc'd for $C_{58}H_{50}N_6F_6P_2Rh_2Cl_2O_8$: C, 49.35; H, 3.57; N, 5.95; Cl, 5.02. MS(FAB): 1001 [L_2Rh(cod)], 668 [LRh(cod)]. Found: C, 49.65; H, 3.71; N, 5.55; Cl, 5.44. ^{19}F NMR ($CDCl_3$): $\delta(F_1$(between imine and F_3))-137.3 ppm (broad, 2F), $\delta(F_2$(between imine and one CN) -114.5 ppm (broad doublet, J = 22 Hz, 2F), $\delta(F_3$(between F_1 and one CN))-130.5 ppm (broad doublet, J = 22 Hz, 2F); ^1H NMR ($CDCl_3$): phenyl rings, δ 7.50, 7.75 ppm (m, 20H); δ 4.65 ppm (s, 8H, HC=), δ 2.60

ppm (broad, 8H, H_2C-), δ 2.00 ppm (broad, 8H, H_2C-), methyl groups: δ 2.30 ppm (d, 6H, $^2J_{PH} = 13$ Hz). Molecular weight determination: 828 (solvent: CH_2Br_2).

Synthesis of



$[(cod)Rh\text{-}1\text{-}(\pi\text{-}CN)\text{-}C_6F_2\text{-}4\text{-}(\pi\text{-}CN)Rh(cod)\text{-}4'\text{-}(\pi\text{-}CN)\text{-}C_6F_2\text{-}1'\text{-}(\pi\text{-}CN)]^{2+}(ClO_4^-)_2$

(2-16):

To a 100 ml flask were added $[Rh(cod)Cl]_2$ (0.049 g; 0.100 mmol), $AgClO_4$ (0.042 g; 0.200 mmol) and 15 ml acetone. The solution was stirred for 15 mins, and then the solution was filtered and transferred to a flask in which contains C_6F_4-1,2-$(CN)_2$ (0.040 g; 0.200 mmol) in 15 ml acetone. The resultant yellow solution was stirred at room temperature for about 2h before the solvent was removed *in vacuo* to leave a yellow solid. The crude product was washed with hexane (3x15ml) and dried *in vacuo* to obtain pure compound **2-16**. (yield 0.054g; 53%; mp: > 80 °C decomp). Anal. Calc'd for $C_{16}H_{12}N_2F_4PRhClO_4$: C, 37.63; H, 2.37; N, 5.49; Cl, 6.94. MS(FAB): 411([LRh(cod)]), 503 ([L_2Rh]), 623 ([$LRh_2(cod)_2$]). Found: C, 38.11; H, 2.91; N, 5.73; Cl, 7.52. ^{19}F NMR ($CDCl_3$): -124.3 ppm (broad doublet, J = 10.5 Hz, 1F), -139.2 ppm (broad doublet, J = 10.5 Hz, 1F); ^1H NMR (CD_2Cl_2): phenyl rings, δ 7.7 ppm (m, 15H); cod group: δ 4.50 ppm (broad, 4H, HC=), δ 2.55 ppm (broad, 4H, H_2C-), δ 1.95 ppm (broad, 4H, H_2C-). Molecular weight determination: 835 (solvent: CH_2Br_2).

Synthesis of 3,5,6-trifluoro-2-(triphenylphosphinimino)-*p*-benzoquinone (3-1):

To a solution of 1,4-tetrafluorobenzoquinone (1.00 g, 5.55 mmol) in CH_2Cl_2 (40 ml) maintained at 0 °C using an ice/water bath, was added dropwise a solution of $Me_3SiN{=}PPh_3$ (1.941 g, 5.55 mmol), also in CH_2Cl_2 (20 ml). A purple color formed immediately. The reaction mixture was stirred at 0 °C for about 1h, then at room temperature for 12h. The solution was taken to dryness in vacuum and the resultant purple solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 2.18 g; 90%; purple powder). Anal. Calc'd for $C_{24}H_{15}NF_3O_2P$: C, 65.91; H, 3.46; N, 3.20. MS (EI, m/z): 437 (M+, 100 %). Found: C, 65.22; H, 3.37; N, 3.34. ^{19}F NMR ($CDCl_3$): δ(F_1(*ortho* to N=PPh_3)) -152.55 (d, 1F, $^5J_{F_1\text{-}F_3}$ = 3.8 Hz), δ(F_2(*para* to N=PPh_3)) -141.92 (d, 1F, $^3J_{F_2\text{-}F_3}$ = 7.5 Hz), δ(F_3(*meta* to N=PPh_3)) -148.35 (dd, 1F, $^3J_{F_2\text{-}F_3}$ = 7.5 Hz, $^5J_{F_1\text{-}F_3}$ = 3.8 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.45, 7.80 (m, 15H).

Synthesis of 3,5,6-trifluoro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (3-2):

To a solution of 1,4-tetrafluorobenzoquinone (1.00 g, 5.55 mmol) in CH_2Cl_2 (40 ml) maintained at 0 °C using an ice/water bath, was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (1.560 g, 5.55 mmol), also in CH_2Cl_2 (20 ml). A purple color formed immediately. The reaction mixture was stirred at 0 °C for about 1h, then at room temperature for 12h. The solution was taken to dryness in vacuum and the resultant purple solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 1.10 g; 56 %; purple powder). Anal. Calc'd for $C_{19}H_{13}NF_3O_2P$: C, 60.81; H, 3.49; N, 3.73. MS (EI, m/z): 475 (M+, 100%). Found: C, 59.67; H, 3.31; N, 4.33. ^{19}F NMR ($CDCl_3$): δ(F_1(*ortho* to N=PPh_3)) -154.30 (s, 1F), δ(F_2(*para* to N=PPh_3)) -141.00 (d, 1F, $^3J_{F_2\text{-}F_3}$ = 3.8 Hz), δ(F_3(*meta* to N=PPh_3)) -148.90 (d, 1F, $^3J_{F_2\text{-}F_3}$ = 3.8 Hz). ^1H NMR ($CDCl_3$): phenyl rings δ 7.45, 7.80 (m, 10H), methyl group δ 2.30 (d, 3H, $^2J_{P\text{-}H}$ = 16.0 Hz).

Synthesis of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (3-3):

To a solution of 1,4-tetrachlorobenzoquinone (2.500 g, 10.17 mmol) in THF (80 ml) at RT was added dropwise a solution of $Me_3SiN{=}PPh_3$ (3.554 g, 10.17 mmol), also in THF (20 ml). The reaction mixture was refluxed 12h. The deep blue solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 4.25 g; 88%; blue powder; mp: 227-9 °C). Anal. Calc'd for $C_{24}H_{15}NCl_3O_2P$: C, 59.23; H, 3.11; N, 2.88; Cl, 21.85. MS (EI, m/z): 487 (M+, 100 %). Found: C, 59.19; H, 3.09; N, 2.86; Cl, 21.80. ^1H NMR ($CDCl_3$): phenyl rings δ 7.55, 7.70 (m, 15H).

Synthesis of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (3-4):

To a solution of 1,4-tetrachlorobenzoquinone (2.567 g, 10.44 mmol) in THF (40 ml) at RT was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (3.00 g, 10.44 mmol), also in THF (10 ml). The reaction mixture was refluxed for 12h. The deep blue solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 2.30 g; 52 %; blue powder; mp: 208-210 °C). Anal. Calc'd for $C_{19}H_{13}NCl_3O_2P$: C, 53.74; H, 3.09; N, 3.30; Cl, 25.05. MS (EI, m/z): 425 (M+, 100%). Found: C, 53.73; H, 3.17; N, 3.54; Cl, 23.82. ^1H NMR ($CDCl_3$): phenyl rings δ 7.55, 7.85 (m, 10H), methyl group δ 2.35 (d, 3H, $^2J_{P\text{-}H}$ = 16.0 Hz).

Synthesis of 3,5,6-trichloro-2-(dimethylphenylphosphinimino)-*p*-benzoquinone (3-5):

To a solution of 1,4-tetrachlorobenzoquinone (0.436 g, 1.78 mmol) in THF (25 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPhMe_2$ (0.400 g, 1.78 mmol) also in THF (10 ml). The reaction mixture was refluxed 12h. The deep blue solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3). The product was recrystallized from CH_2Cl_2 and hexane and dried in vacuum to obtain one fourth dichloromethane solvate of (**3-5**). (Yield 0.52 g; 81 %; blue powder). Anal. Calc'd for $C_{14}H_{11}NCl_3O_2P \cdot 1/4CH_2Cl_2$: C, 44.59; H, 3.02; N, 3.65; Cl, 32.33. MS (EI, m/z): 361 (M+, 100%). Found: C, 44.63; H, 2.76; N, 3.76; Cl, 32.54. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.55, 7.80 (m, 5H), methyl groups δ 1.75 (d, 3H, $^2J_{P\text{-}H}$ = 16.0 Hz), δ 2.02 (d, 3H, $^2J_{P\text{-}H}$=16.0 Hz).

Synthesis of 3,6-difluoro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone (3-6):

To a solution of $Me_3SiN{=}PPh_3$ (1.09g, 3.11 mmol) in CH_2Cl_2 (25 ml) maintained at 0 °C with an ice/water bath was added dropwise a solution of 1,4-tetrafluorobenzoquinone (0.280 g, 1.56 mmol), also in CH_2Cl_2 (20 ml). The color of the solution slowly changed from deep purple to green. The reaction mixture was stirred at 0 °C for about 1h, then at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum to obtain the one eighth dichloromethane solvate of **3-6**. (Yield 0.90 g; 82%; green powder; mp: >330 °C, decomp.). Anal. Calc'd for $C_{42}H_{30}N_2F_2O_2P_2 \cdot 1/8\ CH_2Cl_2$: C, 71.74; H, 4.32; N, 3.97; Cl, 1.26. MS (EI, m/z): 694 (M+, 100%). Found: C, 71.55; H, 4.25; N, 4.08; Cl, 1.56. ^{19}F NMR ($CDCl_3$): δ -156.69 (s, 2F). ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.50, 7.80 (m, 30H).

Synthesis of 3,6-difluoro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzoquinone (3-7):

To a solution of $Me_3SiN{=}PPh_2Me$ (1.60 ml, 5.55 mmol) in CH_2Cl_2 (25 ml) maintained at 0 °C with an ice/water bath was added dropwise a solution of 1,4-tetrafluorobenzoquinone (0.500 g, 2.78 mmol), also in CH_2Cl_2 (20 ml). The color of the solution slowly changed from deep purple to green. The reaction mixture was stirred at 0 °C for about 1h, then at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum to obtain the one eighth dichloromethane solvate of **3-7**. (Yield 1.46 g; 90%; green powder; mp: >300 °C, decomp.). Anal. Calc'd for $C_{32}H_{26}N_2F_2O_2P_2 \cdot 1/8\ CH_2Cl_2$: C, 66.40; H, 4.55; N, 4.82; Cl, 1.53. MS (EI, m/z): 570 (M+, 100%). Found: C, 66.20; H, 4.45; N, 5.47; Cl, 1.94. ^{19}F NMR ($CDCl_3$): δ -159.01 (s, 2F). ^{1}H NMR ($CDCl_3$): δ 7.4, 7.7, (m, 20H); δ 2.30 (d, 6H, $^{2}J_{P\text{-}H}$ = 12.0 Hz).

Synthesis of 3,6-difluoro-2,5-bis(dimethylphenylphosphinimino)-*p*-benzoquinone (3-8):

To a solution of $Me_3SiN{=}PPhMe_2$ (1.25 g, 5.55 mmol) in CH_2Cl_2 (25 ml) maintained at 0 °C with an ice/water bath was added dropwise a solution of 1,4-tetrafluorobenzoquinone (0.500 g, 2.78 mmol), also in CH_2Cl_2 (20 ml). The color of the solution slowly changed from deep purple to green. The reaction mixture was stirred at 0 °C for about 1h, then at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum to obtain the one eighth dichloromethane solvate of **3-8**. (Yield 1.46 g; 90 %; green powder; mp: >300 °C, decomp.). Anal. Calc'd for $C_{22}H_{22}N_2F_2O_2P_2 \cdot 1/8\ CH_2Cl_2$: C, 58.15; H, 4.91; N, 6.13; Cl, 1.94. MS (EI, m/z): 446 (M+, 100%). Found: C, 58.65; H, 4.95; N, 6.92; Cl, 1.62. ^{19}F NMR ($CDCl_3$):

δ -160.47 (s, 2F). ^{1}H NMR ($CDCl_3$): phenyl rings: δ 7.45, 7.75, (m, 10H); methyl groups: δ 1.72 (d, 6H, $^2J_{P\text{-}H}$ = 13.3 Hz), δ 2.0 (d, 6H, $^2J_{P\text{-}H}$ = 13.3 Hz).

Synthesis of 3,6-difluoro-2,5-{N=P(Ph)$_2$CH$_2$P(Ph)$_2$}$_2$-*p*-benzoquinone (3-9):

To a solution of $Me_3SiN=P(Ph)_2CH_2P(Ph)_2$ (0.921 g, 1.953 mmol) in CH_2Cl_2 (20 ml) maintained at 0 °C with an ice/water bath was added dropwise a solution of 1,4-tetraflurobenzoquinone (0.176 g, 0.977 mmol), also in CH_2Cl_2 (20 ml). The reaction mixture was stirred at 0 °C for about 1h, and then at room temperature for 12h. The volume of the solution was reduced to about 10 ml, then hexane (15 ml) was introduced via a syringe in order to precipitate the products. The resultant solids were collected by filtration and washed with hexane (20 ml x3) and then dried in vacuum to obtain the three quarters dichloromethane solvate of **3-9**. (Yield, 0.417 g; 43%; green powder). Anal. Calc'd for $C_{56}H_{44}N_2F_2O_2P_4 \cdot 3/4\ CH_2Cl_2$: C, 67.99; H, 4.57; N, 2.79; Cl, 5.30. MS (EI, m/z): 938 (M+, 100 %). Found: C, 67.86; H, 4.65; N, 2.74; Cl, 4.86. ^{19}F NMR ($CDCl_3$): δ -158.59 ppm (s). ^{1}H NMR ($CDCl_3$): δ 7.1 ppm, 7.4 ppm, 7.8 ppm (m, 40 H), 3.7 ppm (m, 4H).

Synthesis of 3,6-dichloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone (3-10):

To a solution of $Me_3SiN=PPh_3$ (1.371 g, 3.92 mmol) in toluene (25 ml) at room temperature was added dropwise a solution of 1,4-tetrachlorobenzoquinone (0.500 g, 1.96 mmol), also in toluene (20 ml). The color of the solution slowly changed from deep blue to green. The reaction mixture was refluxed for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3). The product was recrystallized from CH_2Cl_2 and hexane and dried in vacuum. (Yield 1.65 g; 81%; green powder; mp: 200-2 °C). Anal. Calc'd for

$C_{42}H_{30}N_2Cl_2O_2P_2$: C, 69.34; H, 4.16; N, 3.85; Cl, 9.75. MS (EI, m/z): 726 (M+, 100%). Found: C, 69.33; H, 4.16; N, 3.91; Cl, 9.85. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.50, 7.80 (m, 30H).

Synthesis of 3,6-dichloro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzoquinone (3-11):

To a solution of $Me_3SiN{=}PPh_2Me$ (1.200 g, 4.18 mmol) in toluene (25 ml) at room temperature was added dropwise a solution of 1,4-tetrachlorobenzoquinone (0.513 g, 2.09 mmol) also in toluene (20 ml). The color of the solution slowly changed from deep blue to green. The reaction mixture was refluxed for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3). The product was recrystallized from CH_2Cl_2 and hexane and dried in vacuum to obtain the one eighth dichloromethane solvates of **3-11**. (yield 1.20 g; 94%; green powder; mp: 180-4 °C). Anal. Calc'd for $C_{32}H_{26}N_2Cl_2O_2P_2 \cdot 1/8\ CH_2Cl_2$: C, 62.84; H, 4.31; N, 4.56; Cl, 12.99. MS (EI, m/z): 602 (M+, 100%). Found: C, 63.19; H, 4.37; N, 4.68; Cl, 12.83. ^{1}H NMR ($CDCl_3$): δ 7.35, 7.75, (m, 20H); δ 2.30 (d, 6H, $^2J_{P\text{-}H} = 12.0$ Hz).

Synthesis of 3,6-difluoro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone (3-12):

To a solution of **3-1** (0.457 g, 1.04 mmol) in CH_2Cl_2 (30 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (0.300 g, 1.04 mmol) also in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum to obtain the one eighth dichloromethane solvate of **3-12**. (Yield 0.46 g; 69 %; green powder; mp: 204-6 °C). Anal. Calc'd for $C_{37}H_{28}N_2F_2O_2P_2 \cdot 1/8\ CH_2Cl_2$: C, 69.33; H, 4.43; N, 4.36; Cl,

1.38. MS (EI, m/z): 632 (M+, 100%). Found: C, 69.33; H, 4.45; N, 4.52; Cl, 0.78. ^{19}F NMR ($CDCl_3$): δ -157.43 ppm, (d, 1F), δ -158.20 ppm, (d, 1F), $^5J_{F-F} = 7.5$ Hz. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.50, 7.80 (m, 25H), methyl group δ 2.30 (d, 3H, $^2J_{P-H} = 16.0$ Hz).

Synthesis of 3,6-difluoro-2-(triphenylphosphinimino)-5-(dimethylphenylphosphinimino)-*p*-benzoquinone (3-13):

To a solution of **3-1** (0.582 g, 1.33 mmol) in CH_2Cl_2 (30 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (0.300 g, 1.33 mmol), also in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum to obtain the one eighth dichloromethane solvate of **3-13**. (yield 0.60 g; 78%; green powder). Anal. Calc'd for $C_{32}H_{26}N_2F_2O_2P_2 \cdot 1/8\ CH_2Cl_2$: C, 66.40; H, 4.55; N, 4.82; Cl, 1.53. MS (EI, m/z): 570 (M+, 100%). Found: C, 65.38; H, 4.74; N, 5.09; Cl, 0.75. ^{19}F NMR ($CDCl_3$): δ -157.96 ppm, (d, 1F), δ -159.10 ppm, (d, 1F), $^5J_{F-F} = 7.5$ Hz. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.45, 7.80 (m, 20H), methyl groups δ 1.75 (d, 3H, $^2J_{P-H} = 16.0$ Hz), δ 2.00 (d, 3H, $^2J_{P-H} = 16.0$ Hz).

Synthesis of 3,6-difluoro-2-(methyldiphenylphosphinimino)-5-(dimethylphenylphosphinimino)-*p*-benzoquinone (3-14):

To a solution of **3-2** (0.333 g, 0.89 mmol) in CH_2Cl_2 (30 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPhMe_2$ (0.200 g, 0.89 mmol) also in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 0.37 g; 82%; green powder). Anal. Calc'd for $C_{27}H_{24}N_2F_2O_2P_2$: C, 63.78; H, 4.76; N, 5.51. MS (EI, m/z): 508 (M+, 100%). Found: C, 63.55; H, 4.71; N, 5.71. ^{19}F NMR ($CDCl_3$): δ -159.54 ppm, (d, 1F), δ -159.90 ppm, (d, 1F), $^5J_{F-F} = 7.5$ Hz. ^{1}H NMR ($CDCl_3$): phenyl rings δ 7.50, 7.75 (m, 15H), methyl groups δ 2.05 (d, 3H, $^2J_{P-H} = 13.0$ Hz), δ 1.78 (d, 3H, $^2J_{P-H} = 13.5$ Hz).

Synthesis of 3,6-difluoro-2-{N=P(Ph)$_2$CH$_2$P(Ph)$_2$}-5-(triphenylphosphinimino)-*p*-benzoquinone (3-15):

To a solution of **3-1** (1.001 g, 2.12 mmol) in CH_2Cl_2 (25 ml) at room temperature was added dropwise a solution of $Me_3SiN=PPh_2CH_2PPh_2$ (0.929 g, 2.12 mmol) also in CH_2Cl_2 (25 ml). The reaction mixture was stirred at room temperature for 12h and then the solution was taken to dryness in vacuum and the solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 1.50 g; 90%; deep green powder). Anal. Calc'd for $C_{44}H_{37}N_2F_2O_2P_3$: C, 72.06; H, 4.57; N, 3.43. MS (EI, m/z): 816 (M+, 100 %). Found: C, 71.26; H, 4.54; N, 3.49. ^{19}F NMR ($CDCl_3$): δ -157,43 ppm (d), δ -157.85 ppm (d), $^5J_{F-F} = 7.5$ Hz. ^{1}H NMR ($CDCl_3$): phenyl rings: δ 7.10, 7.45, 7.80 ppm (m, 40H). methylene group: δ 3.66 ppm (d, 2H, $^2J_{P-H} = 12.8$ Hz).

Synthesis of 3,6-dichloro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone (3-16):

To a solution of **3-3** (0.500 g, 1.06 mmol) in THF (30 ml) at room temperature was added dropwise a solution of $Me_3SiN=PPh_2Me$ (0.350 g, 1.22 mmol) also in THF (10 ml). The reaction mixture was stirred at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 0.61 g; 87%; green powder). Anal. Calc'd for $C_{37}H_{28}N_2Cl_2O_2P_2$: C, 66.78; H, 4.24; N, 4.21; Cl, 10.65. MS (EI, m/z): 664 (M+, 100%). Found: C, 66.82; H, 4.24; N, 4.23; Cl, 10.61. ^{1}H NMR

($CDCl_3$): phenyl rings δ 7.45, 7.85 (m, 25H), methyl group δ 2.40 (d, 3H, $^2J_{P-H}$ = 16.0 Hz).

Synthesis of Bis{diphenyl(N, N'-2,5-difluoro-4-(triphenylphosphinimino)-2,5-cyclohexadiene-3,6-dione)imino-phosphino}-methane (3-17):

To a solution of compound **3-1** (0.223 g, 0.509 mmol) in CH_2Cl_2 (15 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPh_2CH_2P(Ph_2){=}NSiMe_3$ (0.142 g, 0.255 mmol) also in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 12h. The deep green solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum to obtain the 1:1 dichloromethane solvate of **3-17**. (Yield, 0.26 g; 77%; green powder). Anal. Calc'd for $C_{73}H_{52}N_4F_4O_4P_4 \cdot CH_2Cl_2$: C, 66.68; H, 4.08; N, 4.20; Cl, 5.32. MS (FAB): 1250 (M+, 100 %). Found: C, 66.72; H, 4.09; N, 5.03. Cl, 5.37. ^{19}F NMR ($CDCl_3$): δ -156.31 ppm (d), δ -157.60 ppm (d), $^5J_{F-F}$ = 7.5 Hz. ^1H NMR ($CDCl_3$): δ 7.0 ppm, 7.5 ppm, 7.8 ppm (m, 50 H), methylene group: δ 3.5 ppm (d, 2H, $^2J_{P-H}$ = 13 Hz).

Synthesis of [3,5,6-trifluoro-2-(triphenylphosphinimino)-*p*-benzoquinone) {σ-O, N}Rh(cod)](ClO_4) (3-18):

To a 100 ml Schlenk flask were added $[(cod)RhCl]_2$ (0.049 g, 0.100 mmol), $AgClO_4$ (0.042 g, 0.20 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-1** (0.088 g, 0.200 mmol), also in acetone (15 ml), and the mixed solutions were stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a precipitate formed. The product was filtered and washed with hexane (10 ml x 2). The product was recrystallized from

CH_2Cl_2 and hexane and dried in vacuum to obtain the one eighth dichloromethane solvate of **3-18**. (yield: 0.11 g; 73%; brown powder). Anal. Calc'd for $C_{32}H_{27}NClF_3O_6PRh{\cdot}1/8CH_2Cl_2$: C, 50.87; H, 3.62; N, 1.85; Cl, 5.84. MS (FAB): 648 (monocation). Found: C, 49.06; H, 3.63; N, 1.87; Cl, 5.65. ^{19}F NMR ($CDCl_3$): δ -140.43 ppm (dd, 1F, coupling constant: 1.5 Hz and 4.9 Hz), δ -148.33 ppm (d, 1F, coupling constant: 4.9 Hz), δ -158.76 ppm (s, 1F). ^1H NMR ($CDCl_3$): phenyl rings: δ 7.55, 7.65 ppm (m, 15H), cod groups: δ 4.20 ppm (s, 4H, HC=), δ 2.45 ppm (m, 4H, H_2C), δ 1.65 ppm (broad, 4H, H_2C).

Synthesis of [3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone){σ-O, N}Rh(cod)](ClO_4) (3-19):

To a 100 ml Schlenk flask were added $[(cod)RhCl]_2$ (0.049 g, 0.100 mmol), $AgClO_4$ (0.042 g, 0.20 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-4** (0.085 g, 0.200 mmol), also in acetone (15 ml), and the mixed solutions were stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a precipitate formed. The product was filtered and washed with hexane (10 ml x 2) and dried in vacuum. (yield: 0.102 g; 69%; brown powder). Anal. Calc'd for $C_{27}H_{25}NCl_4O_6PRh$: C, 44.11; H, 3.43; N, 1.91; Cl, 19.29. MS (FAB): 636 (monocation). Found: C, 44.08; H, 3.49; N, 1.93; Cl, 17.96. M.W.: 511.4 (solvent: CH_2Br_2). ^1H NMR ($CDCl_3$): phenyl rings: δ 7.60, 7.80 ppm (m, 10H), cod groups: δ 4.23 ppm (s, 4H, HC=), δ 2.50 ppm (m, 4H, H_2C), δ 1.70 ppm (broad, 4H, H_2C). Methyl group: δ 2.80 ppm (d, $^2J_{P\text{-}H}$ = 12 Hz).

Synthesis of [π-(3,6-difluoro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone)Rh(cod)](ClO$_4$) (3-20):

To a 100 ml Schlenk flask were added [(cod)RhCl]$_2$ (0.025 g, 0.05 mmol), AgClO$_4$ (0.021 g, 0.10 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-6** (0.070 g, 0.100 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH$_2$Cl$_2$ and ether, and then dried in vacuum to obtain the one quarter dichloromethane solvate of **3-20**. (yield: 0.080 g; 80%; brown powder; mp: > 300 °C). Anal. Calc'd for $C_{50}H_{42}N_2ClF_2O_6P_2Rh \cdot 1/4\ CH_2Cl_2$: C, 58.80; H, 4.17; N, 2.73; Cl, 5.18. MS (FAB): 906.4 (monocation, LRh(cod)$^+$). Found: C, 58.90; H, 4.14; N, 2.96; Cl, 4.45. ^{19}F NMR (CDCl$_3$): δ -178.1 ppm (d), $^2J_{F\text{-}Rh}$ = 10.2 Hz. ^{1}H NMR (CDCl$_3$): phenyl rings: δ 7.45, 7.55, 7.70, 7.85 ppm (m, 30H). cod groups: δ 4.25 ppm (broad, 4H, HC=), δ 2.50 ppm (m, 4H, H$_2$C), δ 1.75 ppm (broad, 4H, H$_2$C).

Synthesis of {π-[3,6-difluoro-2,5-bis(methyldiphenylphosphinimino)-*p*-benzo-quinone]Rh(cod)}(ClO$_4$) (3-21):

To a 100 ml Schlenk flask were added [(cod)RhCl]$_2$ (0.025 g, 0.05 mmol), AgClO$_4$ (0.021 g, 0.10 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-7** (0.058 g, 0.10 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for 1h. The solution was then taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystalized from CH_2Cl_2 and ether, and dried in vacuum to obtain the one quarter dichloromethane solvate of **3-21**. (yield: 0.070 g; 78%; brown powder). Anal. Calc'd for $C_{40}H_{38}N_2ClF_2O_6P_2Rh{\cdot}1/4\ CH_2Cl_2$: C, 53.58; H, 4.30; N, 3.10; Cl, 5.89. MS (FAB): 781 (monocation, $LRh(cod)^+$). Found: C, 52.89; H, 4.01; N, 3.50; Cl, 5.12. ^{19}F NMR ($CDCl_3$): δ -178.3 ppm (d). $^2J_{F\text{-}Rh}$=10.2 Hz. ^1H NMR ($CDCl_3$): Phenyl rings: δ 7.50 ppm, 7.70 ppm (m, 20 H); cod groups: δ 4.15 ppm (broad, 4H, HC=), δ 2.45 ppm (broad, 4H, H_2C), δ 1.60 ppm (broad, 4H, H_2C). Methyl groups: 2.05 (d, 6H, $^2J_{P\text{-}H}$ = 16 Hz).

Synthesis of {π-[3,6-difluoro-2-(methyldiphenylphosphinimino)-5-(triphenylphosphinimino)-*p*-benzoquinone]Rh(cod)}(ClO_4) (3-22):

To a 100 ml Schlenk flask were added $[(cod)RhCl]_2$ (0.025 g, 0.05 mmol), $AgClO_4$ (0.021 g, 0.10 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-12** (0.064 g, 0.100 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for about 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 and ether, and then dried in vacuum to obtain the one quarter dichloromethane solvate of **3-22**. (yield: 0.070 g; 73%; brown powder). Anal. Calc'd for $C_{45}H_{40}N_2ClF_2O_6P_2Rh.1/4CH_2Cl_2$: C, 56.36; H, 4.23; N, 2.90; Cl, 5.51. MS (FAB): 843 (monocation, $LRh(cod)^+$). Found: C, 56.60; H, 4.13; N, 2.80; Cl, 5.65. ^{19}F NMR ($CDCl_3$): δ -178.4 ppm (dd), δ -179.1 ppm (dd), $^2J_{F\text{-}Rh}$ = 10.2 Hz, $^5J_{F\text{-}F}$ = 3 Hz. ^1H NMR ($CDCl_3$): Phenyl rings: δ 7.5 ppm, 7.7 ppm (m, 20 H); cod groups: δ 4.25 ppm (broad, 4H, HC=), δ 2.50 ppm (broad, 4H, H_2C), δ 1.70 ppm (broad, 4H, H_2C). Me groups: 2.10 (m, 6H).

Synthesis of {π-[3,6-dichloro-2-(triphenylphosphinimino)-5-(methyldiphenylphosphinimino)-*p*-benzoquinone]Rh(cod)}(ClO_4) (3-23):

To a 100 ml Schlenk flask were added [(cod)RhCl]$_2$ (0.049 g, 0.100 mmol), $AgClO_4$ (0.042 g, 0.200 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-16** (0.067 g, 0.100 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown-red. The mixture was stirred for about 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown-red precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 and ether, and then dried in vacuum. (yield: 0.076 g; 78%; brown powder). Anal. Calc'd for $C_{45}H_{40}N_2Cl_3O_6P_2Rh$: C, 55.38; H, 4.13; N, 2.87; Cl, 10.90. MS (FAB): 875 (monocation). Found: C, 54.80; H, 4.59; N, 2.71; Cl, 10.17. ^1H NMR ($CDCl_3$): phenyl rings: δ 7.60, 7.85 ppm (m, 25H), methyl group: δ 2.65 ppm (d, 3H, $^2J_{P-H}$ = 16 Hz), cod group: δ 4.85 ppm (broad, 4H, HC=), δ 2.45 ppm (broad, 4H, H_2C), δ 2.18 ppm (broad, 4H, H_2C).

Synthesis of {π, π'-[Bis(diphenyl (N, N'-2,5-difluoro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dione)imino-phosphino) methane]$Rh_2(cod)_2$}$(ClO_4)_2$ (3-24):

To a 100 ml Schlenk flask were added [(cod)RhCl]$_2$ (0.034 g, 0.069 mmol), $AgClO_4$ (0.029 g, 0.137 mmol) and acetone (15 ml). The mixture was stirred for 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **3-17** (0.086 g, 0.069 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for about 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 and ether, and then dried in vacuum. (yield: 0.080 g; 62%; brown powder). Anal. Calc'd for $C_{89}H_{76}N_4Cl_2F_4O_{12}P_4Rh_2$: C, 57.16; H, 4.10; N, 3.00; Cl, 3.79. MS (FAB): 1460 ($LRh(cod)^+$). Found: C, 56.78; H, 3.90; N, 3.15; Cl, 3.57. ^{19}F NMR ($CDCl_3$): δ -175.4 ppm (dd), δ -175.7 ppm (dd), $^2J_{F\text{-}Rh}$ = 10.5 Hz, $^5J_{F\text{-}F}$=3.0 Hz. ^1H NMR ($CDCl_3$): phenyl rings: δ 7.65, 7.95 ppm (m, 50H), methylene in PCH_2P: δ 5.20 ppm (m, 2H), cod group: δ 4.20 ppm (m, 8H, HC=), δ 2.45 ppm (broad, 8H, H_2C), δ 1.75 ppm (broad, 8H, H_2C).

Synthesis of 3-chloro-2-(triphenylphosphinimino)-*p*-naphthoquinone (3-25):

To a solution of 2,3-dichloro-*p*-naphthoquinone (0.500 g, 2.20 mmol) in CH_2Cl_2 (50 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPh_3$ (0.77 g, 2.20 mmol), also in CH_2Cl_2 (20 ml). The reaction mixture was stirred at room temperature for 12h. The deep red solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in vacuum. (Yield 0.74 g; 72 %; red powder; mp: 168-9 °C). Anal. Calc'd for $C_{28}H_{19}NClO_2P$: C, 71.88; H, 4.09; N, 2.99; Cl, 7.58. MS (EI, m/z): 467 (M+, 100 %). Found: C, 71.01; H, 4.08; N, 3.05; Cl, 7.98. ^1H NMR ($CDCl_3$): phenyl rings δ 7.55, 7.70 (m, 15H).

Synthesis of 3-chloro-2-(methyldiphenylphosphinimino)-*p*-naphthoquinone (3-26):

To a solution of 2,3-dichloro-*p*-naphthoquinone (0.50 g, 2.20 mmol) in CH_2Cl_2 (40 ml) at room temperature was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (0.63 g, 2.20 mmol), also in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 12h. The deep red solution was taken to dryness in vacuum and the resultant solids were washed with hexane (20 ml x 3) and dried in

vacuum. (Yield 0.53 g; 59 %; red powder; mp: 167-8 °C). Anal. Calc'd for $C_{23}H_{17}NClO_2P$: C, 68.07; H, 4.22; N, 3.45; Cl, 8.74. MS (EI, m/z): 405 (M+, 100%). Found: C, 67.59; H, 4.39; N, 3.72; Cl, 9.21. ^1H NMR ($CDCl_3$): phenyl rings δ 7.55, 7.85 (m, 10H), methyl group δ 2.35 (d, 3H, $^2J_{P-H}$ = 16.0 Hz).

Synthesis of 3,6-dichloro-5-(*p*-fluorophenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA1) (4-1):

To a solution of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (0.500 g, 1.10 mmol) in toluene (40 ml) was added dropwise a solution of 4-fluoroaniline (0.250 g, 2.25 mmol), also in toluene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 0.52 g; 84%; green powder; mp: 258-60 °C). Anal. Calc'd for $C_{30}H_{20}N_2Cl_2FO_2P$: C, 64.19; H, 3.59; N, 4.99; Cl, 12.63. MS (EI, m/z): 560 (M+, 100 %). Found: C, 63.37; H, 3.48; N, 4.89; Cl, 12.14. ^{19}F NMR ($CDCl_3$): δ -115.62 ppm (m). ^1H NMR ($CDCl_3$): Ph_3: δ 7.5, 7.8 ppm (m, 15 H); $-C_6H_4-$: δ 7.0 ppm (m, 4 H); N-H: δ 8.25 ppm (s, 1H).

Synthesis of 3,6-dichloro-5-(*p*-chlorophenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA2) (4-2):

To a solution of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (0.456 g, 1.00 mmol) in toluene (30 ml) was added dropwise a solution of 4-chloroaniline (0.260 g, 2.00 mmol), also in toluene (15 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 0.52 g; 90%; green powder; mp: 264-5 °C). Anal. Calc'd for $C_{30}H_{20}N_2Cl_3O_2P$: C, 62.36; H, 3.49; N, 4.85; Cl, 18.41. MS (EI, m/z): 578 (M+, 100 %). Found: C, 62.35; H, 3.47; N, 4.55; Cl, 17.76. ^1H NMR ($CDCl_3$): Ph_3: δ 7.5, 7.8 ppm (m, 15 H); $-C_6H_4-$: δ 7.0, 7.25 ppm (m, 4 H); N-H: δ 8.25 ppm (s, 1H).

Synthesis of 3,6-dichloro-5-(*p*-methylphenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA3) (4-3):

To a solution of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (0.450 g, 0.92 mmol) in toluene (40 ml) was added dropwise a solution of 4-methylaniline (0.200 g, 1.85 mmol), also in toluene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and recrystalized with CH_2Cl_2 and pentane and dried under vacuum to obtain the one-half dichloromethane solvate of **4-3**. (yield 0.30 g; 54%; green powder). Anal. Cald for $C_{31}H_{23}N_2Cl_2O_2P\cdot$ 1/2 CH_2Cl_2: C, 63.07; H, 4.03; N, 4.67; Cl, 17.73. MS (EI, m/z): 556 (M+, 100 %). Found: C, 62.86; H, 3.85; N, 4.65; Cl, 18.23. ^1H NMR ($CDCl_3$): Ph_3: δ 7.5, 7.85 ppm (m, 15 H); $-C_6H_4-$: δ 6.95, 7.10 ppm (m, 4 H); N-H: δ 8.32 ppm (s, 1H); Methyl group: δ 2.3 ppm (s, 3H).

Synthesis of 3,6-dichloro-5-(*p*-NH_2-phenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone, (HQA4) (4-4):

To a solution of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (0.243 g, 0.500 mmol) in toluene (40 ml) was added dropwise a solution of 1,4-phenylenediamine (0.108g, 1.00 mmol), also in toluene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and recrystallized with CH_2Cl_2 and pentane and dried under vacuum to obtain the one-eighth dichloromethane solvate of **4-4**. (yield 0.22 g; 77 %; green powder). Anal. Cald for $C_{30}H_{22}N_3Cl_2O_2P\cdot 1/8\ CH_2Cl_2$: C, 63.59; H, 3.94; N, 7.38; Cl, 14.02. MS (EI, m/z): 557 (M+, 100 %). Found: C, 63.30; H, 4.07; N, 6.82; Cl, 12.96. ^1H NMR ($CDCl_3$): Ph_3: δ 7.5, 7.85 ppm (m, 15 H); $-C_6H_4-$: δ 6.60, 6.90 ppm (m, 4 H); N-H: δ 8.30 ppm (s, 1H).

Synthesis of 3,6-dichloro-5-(*p*-fluorophenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA5) (4-5):

To a solution of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (0.500 g, 1.18 mmol) in benzene (20 ml) was added dropwise a solution of 4-fluroalinine (0.264 g, 2.35 mmol) also in benzene(10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2). The product was recrystallized from CH_2Cl_2 and hexane and dried under vacuum to obtain the one-eighth dichloromethane solvate of **4-5**. (yield 0.58 g; 97%; green powder). Anal. Calc'd for $C_{25}H_{18}N_2Cl_2FO_2P\cdot 1/8CH_2Cl_2$: C, 59.18; H, 3.61; N, 5.38; Cl, 15.64. MS (EI, m/z): 498 (M+, 100 %). Found: C, 58.45; H, 3.76; N, 5.83; Cl, 15.91. ^{19}F NMR ($CDCl_3$): δ -115.60 ppm (m). ^1H NMR ($CDCl_3$): Ph_2: δ 7.5, 7.9 ppm (m, 10 H); $-C_6H_4-$: δ 7.0 ppm (m, 4 H); Me: δ 2.4 ppm (d, 3 H); N-H: δ 8.35 ppm (s, 1H).

Synthesis of 3,6-dichloro-5-(*p*-chlorophenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA6) (4-6):

To a solution of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (0.500 g, 1.18 mmol) in benzene (20 ml) was added dropwise a solution of 4-chloroaniline (0.307 g, 2.35 mmol), also in benzene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2). The product was recrystallized from CH_2Cl_2 and hexane and dried under vacuum to obtain the one-eighth dichloromethane solvate of **4-6**. (yield 0.58 g; 94%; green powder). Anal. Calc'd for $C_{30}H_{20}N_2Cl_3O_2P\cdot 1/8CH_2Cl_2$: C, 57.33; H, 3.49; N, 5.32; Cl, 21.89. MS (EI, m/z): 514 (M+, 100 %). Found: C, 57.29; H, 3.55; N, 5.31; Cl, 21.51. ^1H NMR ($CDCl_3$): Ph_2: δ 7.5, 7.8 ppm (m, 10 H); $-C_6H_4-$: δ 7.0, 7.25 ppm (m, 4 H); Me: δ 2.4 ppm (d, 3 H); N-H: δ 8.30 ppm (s, 1H).

Synthesis of 3,6-dichloro-5-(*p*-methylphenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA7) (4-7):

To a solution of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (0.497 g, 1.17 mmol) in benzene (20 ml) was added dropwise a solution of 4-methylaniline (0.253 g, 2.34 mmol), also in benzene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for overnight. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and recrystallized with CH_2Cl_2 and pentane and dried under vacuum to obtain the one-eighth dichloromethane solvate of **4-7**. (yield 0.38 g; 64%; green powder). Anal. Cald for $C_{26}H_{21}N_2Cl_2O_2P\cdot 1/8\ CH_2Cl_2$: C, 62.02; H, 4.23; N,

5.54; Cl, 15.78. MS (EI, m/z): 494 (M+, 100 %). Found: C, 61.57; H, 4.35; N, 5.61; Cl, 16.06. ^1H NMR ($CDCl_3$): Ph_2: δ 7.5, 7.85 ppm (m, 10 H); -C_6H_4-: δ 6.95, 7.15 ppm (m, 4 H); Me: δ 2.4 ppm (m, 6H); N-H: δ 8.37 ppm (s, 1H);

Synthesis of 3,6-dichloro-5-(*p*-NH_2-phenylamino)-2-(methyldiphenylphosphinimino)-*p*-benzoquinone, (HQA8) (4-8):

To a solution of 3,5,6-trichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (0.500 g, 1.18 mmol) in benzene (20 ml) was added dropwise a solution of 1,4-phenylenediamine (0.255, 2.35 mmol) also in benzene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and recrystallized from CH_2Cl_2 and pentane, and dried on vacuum to obtain the one (H_2N-C_6H_4-NH_3.Cl) co-crystalized and one-quarter dichloromethane solvate of **4-8**. (yield 0.57 g; 73%; green powder). Anal. Calc'd for $C_{25}H_{20}N_3Cl_2O_2P\cdot[H_2N\text{-}C_6H_4\text{-}NH_3.Cl]\cdot 1/8\ CH_2Cl_2$: C, 56.68; H, 4.49; N, 10.58; Cl, 18.74. MS (EI, m/z): 495 (M+, 100 %). Found: C, 56.87; H, 4.33; N, 10.15; Cl, 18.74. ^1H NMR ($CDCl_3$): Ph_2: δ 7.5, 7.85 ppm (m, 10 H); -C_6H_4-: δ 6.60, 6.90 ppm (m, 4 H); Me: δ 2.4 ppm (d, 1H); N-H: δ 8.37 ppm (s, 1H).

Synthesis of 1,4-N,N'-bis(2,5-dichloro-4-(triphenylphosphinimino)-2,5-cyclohexadiene, 3,6-dione)phenyldiamine, (H_2QA9) (4-9):

To a solution of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (1.058 g, 2.17 mmol) in benzene (40 ml) was added dropwise a solution of 1,4-phenylenediamine (0.118 g, 1.09 mmol) and triethylamine (0.220 g, 2.17 mmol) also in benzene (10 ml). The reaction mixture was stirred at room temperature for about 0.5

h, then refluxed for overnight. The solution was cooled down and taken to dryness under vacuum and the green solids were washed with hexane (20 ml x 2), H_2O (20 ml x 2), EtOH (20 ml x 2) and hexane (20 ml x 2) and recrystallized from CH_2Cl_2 and hexane, and dried in vacuum to obtain the one-quarter dichloromethane solvate of **4-9**. (yield 0.61 g; 55%; green powder). Anal. Calc'd for $C_{54}H_{36}N_4Cl_4O_4P_2 \cdot 1/4CH_2Cl_2$: C, 63.27; H, 3.57; N, 5.44; Cl, 15.49. MS (FAB): 1009 (M+, 100 %). Found: C, 63.16; H, 3.46; N, 5.59; Cl, 15.86. ^1H NMR ($CDCl_3$): Ph_3: δ 7.4, 7.8 ppm (m, 30 H); $-C_6H_4-$: δ 6.95, 7.25 ppm (m, 4 H); N-H: δ 8.32 ppm (s, 2H).

Synthesis of 2-(triphenylphosphinimino)-3,5-bis(3,5-dimethyl-pyrazol-1-yl)-6-chlorobenzoquinone (4-10):

To a solution of 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (0.487 g, 1.00 mmol) in THF (20 ml) were added dropwise the solution of trimethylsilyl-3,5-dimethylpyrazole (0.504 g, 3.00 mmol), also in THF (10 ml). The reaction mixture was refluxed for 12h before it was sequentially cooled down, taken to dryness, washed with hexane (10 ml x 3). The product was recrystallized from CH_2Cl_2 and hexane and dried in vacuum to obtain the one and a half dichloromethane solvate of **4-10**. (yield 0.53 g; 72%; brown powder). Anal. Calc'd for $C_{34}H_{29}N_5ClO_2P.3/2CH_2Cl_2$: C, 58.13; H, 4.40; N, 9.55; Cl, 19.33. MS (EI, m/z): 605 (M+, 100 %). Found: C, 59.05; H, 3.73; N, 9.29; Cl, 19.30. ^1H NMR ($CDCl_3$): Ph_3: δ 7.50, 7.85 ppm (m, 15 H); H-C: δ 5.67 ppm (s, 1H), 5.82 ppm (s, 1H); methyl groups: δ 1.50 ppm (s, 3H), δ 1.95 ppm (s, 3H), δ 2.02 ppm (s, 3H), δ 2.20 ppm (s, 3H).

Synthesis of 3-chloro-2-(triphenylphosphinimino)-10H-5-thia-10-azaanthracene-1,4-dione (4-11):

To a 100 ml flask were added 3,5,6-trichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (0.487 g, 1.00 mmol) and zinc 2-aminobenzenethiolate (0.646 g, 2.05 mmol) and then EtOH (99.9%, 50 ml). The reaction mixture was stirred at room temperature for about 0.5 h, then refluxed for 12h. The solution was cooled down and then taken to dryness in vacuum. The solids were then redissolved in CH_2Cl_2, this solution was filtered, and the filtrate was taken to near dryness. Hexane (10 ml) was added, and the precipitate was collected by filtration and dried in vacuum to obtain the one-quarter 2-aminothiophenol and one-eighth dichloromethane solvate of **4-11**. (yield 0.33 g; 57%; brown powder; mp: >300 °C). Anal. Calc'd for $C_{30}H_{20}N_2ClO_2PS\cdot[2\text{-}NH_2\text{-}C_6H_4\text{-}SH]\cdot 1/8CH_2Cl_2$: C, 65.39; H, 3.86; N, 5.43; Cl, 7.63; S, 6.90 MS (EI, m/z): 538 (M+, 100 %). Found: C, 65.83; H, 3.72; N, 5.52; Cl, 7.72; S, 6.88. ^1H NMR ($CDCl_3$): Ph_3: δ 7.45, 7.85 ppm (m, 15 H); $-C_6H_4-$: δ 6.70 ppm (m, 4 H); N-H: δ 8.25 ppm (s, 1H).

Synthesis of $[(QA1)\{\sigma\text{-}O, N{=}PPh_3\}Rh_2(cod)_2](ClO_4)$ (4-12):

To a 100 ml Schlenk flask were added $[(cod)RhCl]_2$ (0.049 g, 0.10 mmol) and $AgClO_4$ (0.042 g, 0.20 mmol), and acetone (15 ml). The mixture was stirred for about 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **4-1** (0.056 g, 0.10 mmol), also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recystallized from CH_2Cl_2 and ether, and dried in vacuum to obtain the one-quarter dichloromethane solvate of **4-12**. (yield: 0.065 g; 59%; brown powder). Anal. Calc'd for

$C_{46}H_{43}N_2Cl_3FO_6PRh_2 \cdot 1/4\ CH_2Cl_2$: C, 50.35 ; H, 3.97 ; N, 2.54 ; Cl, 11.25 . MS (FAB): 982 (monocation). Found: C, 49.16 ; H, 3.79 ; N, 2.44; Cl, 10.54. ^{1}H NMR ($CDCl_3$): Ph_3: δ 7.45, 7.65, 7.85 ppm (m, 15 H); $-C_6H_4-$: δ 7.0 ppm (m, 4H). cod groups: δ 4.25 ppm (s, 8H, HC=), δ 2.45 ppm (broad, 8H), δ 1.70 ppm (broad, 8H, H_2C).

Synthesis of [(QA2) {σ-O, N=PPh$_3$} Rh$_2$(cod)$_2$](ClO$_4$) (4-13):

To a 100 ml Schlenk flask were added $[(cod)RhCl]_2$ (0.049 g, 0.10 mmol) and $AgClO_4$ (0.042 g, 0.20 mmol), and acetone (15 ml). The mixture was stirred for about 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **4-2** (0.058 g, 0.10 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 and ether, and dried in vacuum. (yield: 0.062 g; 56%; brown powder). Anal. Calc'd for $C_{46}H_{43}N_2Cl_4O_6PRh_2$: C, 50.30; H, 3.95; N, 2.55; Cl, 12.91. MS (FAB): 999 (monocation). Found: C, 49.89; H, 4.04; N, 2.16; Cl, 12.00. ^{1}H NMR ($CDCl_3$): Phenyl groups: δ 7.45, 7.55, 7.65 ppm (m, 15H); $-C_6H_4-$: δ 7.0 ppm (m, 4H). cod groups: δ 4.25 ppm (s, 8H, HC=), δ 2.50 ppm (broad, 8H), δ 1.65 ppm (broad, 8H, H_2C).

Synthesis of [(QA3){σ-O, N=PPh$_3$}Rh$_2$(cod)$_2$](ClO$_4$) (4-14):

To a 100 ml Schlenk flask was added $[(cod)RhCl]_2$ (0.049 g, 0.10 mmol) and $AgClO_4$ (0.042 g, 0.20 mmol), and acetone (15 ml). The mixture was stirred for about 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **4-3** (0.060 g, 0.10 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 and ether, and then dried in vacuum to obtain the one-quarter dichloromethane solvate of **4-14**. (yield: 0.076 g; 65%; brown powder). Anal. Calc'd for $C_{47}H_{46}N_2Cl_3O_6PRh_2 \cdot 1/4\ CH_2Cl_2$: C, 48.80; H, 4.03; N, 2.41; Cl, 10.67. MS (FAB): 978 (monocation). Found: C, 49.52; H, 4.06; N, 2.58; Cl, 10.60. ^1H NMR ($CDCl_3$): Ph groups: δ 7.50, 7.65 ppm (m, 15 H); $-C_6H_4-$: δ 7.15 ppm (m, 4H). cod groups: δ 4.25 ppm (broad, 8H, HC=), δ 2.45 ppm (broad, 8H), δ 1.70 ppm (broad, 8H, H_2C). Methyl group: δ 2.30 (s, 3H).

Synthesis of [(HQA3) {σ-O, N=PPh_3} Rh(cod)](ClO_4) (4-15):

To a 100 ml Schlenk flask was added $[(cod)RhCl]_2$ (0.049 g, 0.10 mmol) and $AgClO_4$ (0.042 g, 0.20 mmol), and acetone (15 ml). The mixture was stirred for about 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **4-3** (0.120 g, 0.20 mmol) also in acetone (15 ml). The color immediately changed from green to deep brown. The mixture was stirred for 1h. The solution was taken to near dryness, then ether (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 and ether, and dried in vacuum. (yield: 0.14 g; 81%; brown powder). Anal. Calc'd for $C_{39}H_{35}N_2Cl_3O_6PRh \cdot 1/4CH_2Cl_2$: C, 53.02; H, 4.02; N, 3.15; Cl, 13.95. MS (FAB): 732 (monocation - Cl). Found: C, 51.64; H, 3.76; N, 3.27; Cl, 12.77. ^1H NMR ($CDCl_3$): Phenyl groups: δ 7.50, 7.65, 7.75, 7.80 ppm (m, 15 H); $-C_6H_4-$: δ 7.05 ppm (m, 4H). N-H: δ 8.0 ppm (s, 1H). cod groups: δ 4.22 ppm (broad, 4H, HC=), δ 2.48 ppm (broad, 4H), δ 1.73 ppm (broad, 4H, H_2C). Methyl group: δ 2.35 (s, 3H).

Synthesis of 3,6-difluoro-2,5-bis(*p*-fluorophenylamino)-*p*-benzoquinone (4-16):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of *p*-flurophenylamine (1.1 ml, 11.11 mmol) also in benzene(20 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 1.98 g; 99 %; brown powder, mp: 350 - 352 °C). Anal. Calc'd for $C_{18}H_{10}N_2F_4O_2$: C, 59.68; H, 2.78; N, 7.73. MS (EI, m/z): 362 (M+, 100 %). Found: C, 59.49; H, 2.68; N, 7.74. ^{19}F NMR ($CDCl_3$): δ -119.31 ppm (m, 2F in phenyl ring); δ -149.60 ppm (s, 2F in quinone ring). ^1H NMR ($CDCl_3$): Ph ring: δ 7.25, 7.45 ppm (m, 8 H); N-H: δ 9.15 ppm (s, 2H). ν_{CO}: 1670 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(*p*-chlorophenylamino)-*p*-benzoquinone (4-17):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of *p*-chlorophenylamine (1.45 g, 11.11 mmol) also in benzene(50 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 2.00 g; 91 %; brown powder, mp: 322 - 324 °C). Anal. Calc'd for $C_{18}H_{10}N_2Cl_2F_2O_2$: C, 54.71; H, 2.55; N, 7.09; Cl, 17.94. MS (EI, m/z): 394 (M+, 100 %). Found: C, 54.50; H, 2.47; N, 7.04; Cl, 17.97. ^{19}F NMR ($CDCl_3$): δ -146.33 ppm (s, 2F). ^1H NMR ($CDCl_3$): Ph ring: δ 7.35, 7.45 ppm (m, 8 H); N-H: δ 9.22 ppm (s, 2H). ν_{CO}: 1667 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(*p*-bromophenylamino)-*p*-benzoquinone (4-18):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of *p*-bromophenylamine (1.97 g, 11.11 mmol) also in benzene(50 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 2.63 g; 98 %; brown powder, mp: 314 - 315 °C). Anal. Calc'd for $C_{18}H_{10}N_2Br_2F_2O_2$: C, 44.66; H, 2.08; N, 5.79; Br, 33.01. MS (EI, m/z): 484 (M+, 100 %). Found: C, 44.38; H, 1.93; N, 5.73; Br, 32.58. ^{19}F NMR ($CDCl_3$): δ -145.86 ppm (s, 2F). ^1H NMR ($CDCl_3$): Ph ring: δ 7.25, 7.55 ppm (m, 8 H); N-H: δ 9.20 ppm (s, 2H). ν_{CO}: 1667 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(*p*-iodophenylamino)-*p*-benzoquinone (4-19):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of *p*-iodophenylamine (2.48 g, 11.11 mmol) also in benzene(50 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 3.05 g; 95 %; grey powder, mp: 310 - 312 °C). Anal. Calc'd for $C_{18}H_{10}N_2I_2F_2O_2$: C, 37.40; H, 1.74; N, 4.85. MS (EI, m/z): 578 (M+, 100 %). Found: C, 37.92; H, 1.76; N, 4.83. ^{19}F NMR ($CDCl_3$): δ -145.55 ppm (s, 2F). ^1H NMR ($CDCl_3$): Ph ring: δ 6.90, 7.55 ppm (m, 8 H); N-H: δ 9.17 ppm (s, 2H). ν_{CO}: 1670 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(*p*-methylphenylamino)-*p*-benzoquinone (4-20):

To a solution of tetrafluoro-*p*-benzoquinone (0.39 g, 2.17 mmol) in EtOH (99.9%) (20 ml) was added dropwise a solution of 4-methylphenylamine (0.47 g, 4.38 mmol) also in EtOH (99.9%) (15 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 0.73 g; 95 %; brown powder, mp: 294 - 296 °C). Anal. Calc'd for $C_{20}H_{16}N_2F_2O_2$: C, 67.79; H, 4.55; N, 7.91. MS (EI, m/z): 354 (M+, 100 %). Found: C, 67.57; H, 4.24; N, 7.84. ^{19}F NMR ($CDCl_3$): δ -144.64 ppm (s, 2F). ^1H NMR ($CDCl_3$): Ph ring: δ 7.20 ppm (m, 8H); Methyl groups: δ 2.30 ppm (s, 6H); N-H: δ 9.03 ppm (s, 2H). ν_{CO}: 1664 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(phenylamino)-*p*-benzoquinone (4-21):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of phenylamine (1.1 ml, 11.11 mmol) also in benzene(50 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 1.72 g; 95 %; brown powder, mp: 302 - 304 °C). Anal. Calc'd for $C_{18}H_{12}N_2F_2O_2$: C, 66.26; H, 3.71; N, 8.59. MS (EI, m/z): 326 (M+, 100 %). Found: C, 66.46; H, 3.62; N, 8.63. ^{19}F NMR ($CDCl_3$): δ -147.91 ppm (s, 2F). ^1H NMR ($CDCl_3$): Ph ring: δ 7.15, 7.35 ppm (m, 8 H); N-H: δ 9.12 ppm (s, 2H). ν_{CO}: 1670 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(*p*-nitrophenylamino)-*p*-benzoquinone (4-22):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of 4-chlorophenylamine (1.56 g, 11.11 mmol) also in benzene(50 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 2.22 g; 96 %; brown powder, mp: 292 - 294 °C). Anal. Calc'd for $C_{18}H_{10}N_4F_2O_6$: C, 51.93; H, 2.42; N, 13.46. MS (EI, m/z): 416 (M+, 100 %). Found: C, 51.76; H, 2.55; N, 12.79. ^{19}F NMR ($CDCl_3$): δ -135.30 ppm (t, 3.8 Hz, 2F). ^{1}H NMR ($CDCl_3$): Ph ring: δ 7.45, 8.30 ppm (m, 8 H); N-H: δ 9.67 ppm (s, 2H). ν_{CO}: 1673 cm^{-1} (KBr).

Synthesis of 3,6-difluoro-2,5-bis(*p*-NMe$_2$-phenylamino)-*p*-benzoquinone (4-23):

To a solution of tetrafluoro-*p*-benzoquinone (1.00 g, 5.55 mmol) in benzene (80 ml) was added dropwise a solution of 4-NMe$_2$-phenylamine (1.56 g, 11.11 mmol) also in benzene(50 ml). The reaction mixture was refluxed for 12h. The solution was cooled down and taken to dryness under vacuum and the solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2) and dried under vacuum. (yield 2.14 g; 93 %; deep blue powder, mp: > 380 °C). Anal. Calc'd for $C_{22}H_{22}N_4F_2O_2$: C, 64.07; H, 5.38; N, 13.58. MS (EI, m/z): 412 (M+, 100 %). Found: C, 64.19; H, 5.27; N, 13.49. ^{19}F NMR ($CDCl_3$): δ -154.63 ppm (s, 2F). ^{1}H NMR ($CDCl_3$): Ph ring: δ 6.75, 7.20 ppm (m, 8 H); Methyl groups: δ 1.30 (m, 12 H); N-H: δ 9.67 ppm (s, 2H). ν_{CO}: 1673 cm^{-1} (KBr).

Synthesis of 3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (5-1):

To a solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (1.00 g, 4.41 mmol) in CH_2Cl_2 (160 ml) at 0 °C maintained in an ice/water bath was added dropwise a solution of $Me_3SiN{=}PPh_3$ (1.54 g, 4.41 mmol), also in CH_2Cl_2 (20 ml). A purple color formed immediately. The reaction mixture was stirred at room temperature for 12h. The solution was taken to dryness in vacuum, and the resulting purple solids were washed with hexane (20 ml x 3) and dried in vacuum. (yield 1.63 g; 78%; purple powder; mp: 213-4 °C). Anal. Calc'd for $C_{25}H_{15}N_2Cl_2O_2P$: C, 62.91; H, 3.17; N, 5.87; Cl, 14.86. MS (EI, m/z): 476 (M+, 100 %). Found: C, 62.76; H, 3.18; N, 6.00; Cl, 14.49. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.45, 7.80 (m, 15H).

Synthesis of 3-cyano-5,6-dichloro-2-(methyldiphenylphosphinimino)-*p*-benzoquinone (5-2):

To a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.00 g, 4.41 mmol) in CH_2Cl_2 (160 ml) at 0 °C maintained in an ice/water bath was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (1.39 g, 4.41 mmol), also in CH_2Cl_2 (20 ml). A purple color formed immediately. The reaction mixture was stirred at room temperature for 12h. The solution was taken to dryness in vacuum, and the resulting purple solids were washed with hexane (20 ml x 3) and dried in vacuum. (yield 1.39 g; 76%; purple powder; mp: 262-266 °C). Anal. Calc'd for $C_{20}H_{13}N_2Cl_2O_2P$: C, 57.85; H, 3.16; N, 6.75; Cl, 17.08. MS (EI, m/z): 414 (M+, 100 %). Found: C, 57.53; H, 3.14; N, 7.18; Cl, 17.48. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.50, 7.75 (m, 10H). methyl group: δ 2.05 (d, 3H, $^2J_{P\text{-}H} = 16$ Hz).

Synthesis of 3-cyano-6-chloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone (5-3):

To a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.50 g, 2.20 mmol) in toluene (80 ml) at 0 °C maintained in an ice/water bath was added dropwise a solution of $Me_3SiN=PPh_3$ (1.54 g, 4.41 mmol), also in toluene (20 ml). A purple color formed immediately. The reaction mixture was stirred at room temperature for 0.5h, then reflux for 12h. The solution was taken to dryness in vacuum, and the resulting brown solids were washed with hexane (20 ml x 3), and then dried in vacuum. (yield 1.20 g; 76%; brown powder; mp: > 330 °C decomp.). Anal. Calc'd for $C_{43}H_{30}N_3ClO_2P_2$: C, 71.92; H, 4.21; N, 5.85; Cl, 4.94. MS (EI, m/z): 717 (M+, 100%). Found: C, 71.84; H, 4.26; N, 6.43; Cl, 5.30. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.50, 7.80 (m, 30H).

Synthesis of 3-cyano-6-chloro-5-(*p*-methylphenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone (5-4):

To a solution of 3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone (**5-1**) (0.477 g, 1.00 mmol) in benzene (20 ml) was added dropwise a solution of 4-methylaniline (0.217 g, 2.00 mmol), also in benzene (10 ml). The reaction mixture was stirred at room temperature for about 0.5h, then refluxed for 12h. The solution was cooled down and taken to dryness in vacuum, and the resulting brown solids were washed with hexane (10 ml x 2), H_2O (10 ml x 2), EtOH (10 ml x 2) and hexane (10 ml x 2), and then dried in vacuum. (yield 0.48 g; 88%; brown powder; mp: > 140 °C decomp.). Anal. Calc'd for $C_{32}H_{23}N_3ClO_2P$: C, 70.14; H, 4.23; N, 7.67; Cl, 6.47. MS (EI, m/z): 547 (M+, 100%). Found: C, 69.93; H, 4.30; N, 7.78; Cl, 6.26. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.5, 7.8 ppm (m, 15 H); $-C_6H_4-$: δ 7.0 ppm (m, 4 H); N-H: δ 8.40 ppm (s, 1H); methyl group: δ 2.3 ppm (s, 3H).

Synthesis of [(3-cyano-5,6-dichloro-2-(triphenylphosphinimino)-*p*-benzoquinone){σ-O, N=PPh$_3$}Rh(cod)]$_2$(ClO$_4$)$_2$ (5-5):

In a 100 ml Schlenk flask [(cod)RhCl]$_2$ (0.049 g, 0.100 mmol), AgClO$_4$ (0.042 g, 0.200 mmol), and acetone (15 ml) were mixed and stirred for 15 mins. A light yellow solution and white ppt. formed. The mixture was filtered into a solution of (**5-1**) (0.096 g, 0.200 mmol), also in acetone (15 ml), and the mixture was stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a red-brown precipitate formed. The product was filtered and recrystallized from CH$_2$Cl$_2$ with hexane, and then dried in vacuum to obtain the one-half hexane solvate of **5-5**. (yield: 0.11 g; 68%; red-brown powder; mp: >110 °C decomp.). Anal. Calc'd for $C_{66}H_{54}N_4Cl_6O_{12}P_2Rh_2 \cdot 1/2(C_6H_{14})$: C, 51.20; H, 3.77; N, 3.46; Cl, 13.14. MS (FAB): 1375 (dication, L$_2$Rh$_2$(cod)$_2$), 1165 (L$_2$Rh(cod)), 687 (LRh(cod)). Found: C, 51.19; H, 3.84; N, 3.42; Cl, 12.41. M.W.: 700 (solvent: CH$_2$Br$_2$). ^{1}H NMR (CDCl$_3$): phenyl groups: δ 7.55, 7.75 ppm (m, 30H), cod groups: δ 4.50 ppm (s, 8H, HC=), δ 2.50 ppm (broad, 8H, H$_2$C), δ 1.85 ppm (broad, 8H, H$_2$C). M.W. determination: 700 (solvent: CH$_2$Br$_2$).

Synthesis of {π-[3-cyano-6-chloro-2,5-bis(triphenylphosphinimino)-*p*-benzoquinone]Rh(cod)}(ClO$_4$) (5-6):

In a 100 ml Schlenk flask [(cod)RhCl]$_2$ (0.025 g, 0.05 mmol), AgClO$_4$ (0.021 g, 0.10 mmol), and acetone (15 ml) were mixed and stirred for 15 mins. A light yellow solution and white ppt. formed. The mixture was filtered into a solution of **5-3** (0.072 g, 0.100 mmol) also in acetone (15 ml), and the mixture was stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH$_2$Cl$_2$ with hexane, and then dried in vacuum. (yield: 0.070 g; 68%; brown powder; mp: >200 °C decomp.). Anal. Calc'd for $C_{51}H_{42}N_3Cl_2O_6P_2Rh$: C, 59.55; H, 4.12; N,

4.08; Cl, 6.89. MS (FAB): 928 (monocation). Found: C, 56.20; H, 3.90; N, 4.85; Cl, 7.31. ^{1}H NMR ($CDCl_3$): phenyl groups: δ 7.50, 7.70, 7.85 ppm (m, 30), cod groups: δ 4.25 ppm (broad, 4H, HC=), δ 2.40 ppm (broad, 4H, H_2C), δ 1.75 ppm (broad, 4H, H_2C).

Synthesis of [(3-cyano-6-chloro-5-(*p*-methylphenylamino)-2-(triphenylphosphinimino)-*p*-benzoquinone){σ-O, N=PPh$_3$}Rh(cod)]-(ClO$_4$) (5-7):

In a 100 ml Schlenk flask $[(cod)RhCl]_2$ (0.049 g, 0.100 mmol), $AgClO_4$ (0.042 g, 0.200 mmol), and acetone (15 ml) were mixed and stirred for 15 mins. A light yellow solution and white ppt. formed. the mixture was filtered into a solution of **5-4** (0.055 g, 0.100 mmol), also in acetone (15 ml), and the mixture was stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a brown precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 with hexane, and then dried in vacuum. (yield: 0.065 g; 76%; brown powder; mp: >150 °C decomp.). Anal. Calc'd for $C_{40}H_{35}N_3Cl_2O_6PRh$: C, 55.96; H, 4.11; N, 4.89; Cl, 8.26. MS (FAB): 758 (monocation). Found: C, 55.93; H, 4.47; N, 4.57; Cl, 8.62. ^{1}H NMR ($CDCl_3$): phenyl groups: δ 7.50, 7.60, 7.75 ppm (m, 15H), $-C_6H_4-$: δ 7.0 ppm (m, 4H). cod groups: δ 4.30 ppm (broad, 4H, HC=), δ 2.50 ppm (broad, 4H, H_2C), δ 1.75 ppm (broad, 4H, H_2C), methyl group: δ 2.17 (s,3H). N-H: δ 8.3 ppm (broad, 1H). M.W. determination: the compound did not disolve in the appropriate solvents.

Synthesis of [(2,3-dichloro-5,6-dicyano-1,4-benzoquinone)$_2${N, N}Rh$_2$(cod)$_2$](ClO$_4$)$_2$ (5-8):

In a 100 ml Schlenk flask $[(cod)RhCl]_2$ (0.049 g, 0.100 mmol), $AgClO_4$ (0.042 g, 0.200 mmol), and acetone (15 ml) were mixed and stirred for 15 mins. A light yellow solution and white ppt. formed. The mixture was filtered into a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.045 g, 0.200 mmol), also in acetone (15 ml), and the mixture was stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a yellow precipitate formed. The product was filtered and recrystallized from CH_2Cl_2 with hexane, and then dried in vacuum to obtain the one-half hexane solvate of **5-8**. (yield: 0.085 g; 76%; yellow powder; mp: >200 °C decomp.). Anal. Calc'd for $C_{32}H_{24}N_3Cl_4O_{10}Rh_2 \cdot 1/2(C_6H_{14})$: C, 37.60; H, 2.79; N, 5.01; Cl, 19.02. MS (FAB): 540 (LRh_2(cod)), 436 (LRh(cod)), 329 (LRh). Found: C, 36.80; H, 2.84; N, 4.74; Cl, 17.51. M.W.: 700 (solvent: CH_2Br_2). ^1H NMR ($CDCl_3$): cod groups: δ 4.20 ppm (broad, 8H, HC=), δ 2.50 ppm (broad, 8H, H_2C), δ 1.90 ppm (broad, 8H, H_2C). M.W. determination: the compound did not disolve in the appropriate solvents.

Synthesis of 4,6-dichloro-2-(triphenylphosphinimino)-1,3,5-s-triazine (6-1):

To a solution of cyanuric chloride (1.96 g, 10.6 mmol) in CH_2Cl_2 (40 ml) was added dropwise a solution of $Me_3SiN{=}PPh_3$ (3.71 g, 10.6 mmol), also in CH_2Cl_2 (25 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (20 ml x 3) and then dried in vacuum. (Yield 3.56 g; 79%; white powder). Anal. Calc'd for $C_{21}H_{15}N_4Cl_2P$: C, 59.31; H, 3.56; N, 13.17, Cl, 16.67. MS (EI, m/z): 424 (M+, 100 %). Found: C, 59.01; H, 3.51; N, 12.73, Cl, 16.50. ^1H NMR ($CDCl_3$): phenyl groups δ 7.60, 7.85 (m, 15H).

Synthesis of 4,6-dichloro-2-(methyldiphenylphosphinimino)-1,3,5-s-triazine (6-2):

To a solution of cyanuric chloride (2.59 g, 13.9 mmol) in CH_2Cl_2 (40 ml) was added dropwise a solution of $Me_3SiN{=}PPh_2Me$ (4.00 g, 13.9 mmol), also in CH_2Cl_2 (25 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (20 ml x 3) and then dried in vacuum. (Yield 4.80 g; 95%; white powder). Anal. Calc'd for $C_{16}H_{13}N_4Cl_2P$: C, 52.91; H, 3.61; N, 15.43, Cl, 19.52. MS (EI, m/z): 362 (M+, 100 %). Found: C, 52.70; H, 3.59; N, 15.06, Cl, 20.03. ^1H NMR ($CDCl_3$): phenyl groups δ 7.50, 7.80 (m, 10H), Methyl group: δ 2.35 ppm (d, 3H, $^2J_{PH}$ = 16 Hz).

Synthesis of 4,6-dichloro-2-($N{=}PPh_2CH_2PPh_2$)-1,3,5-s-triazine (6-3):

To a solution of cyanuric chloride (1.18 g, 6.39 mmol) in CH_2Cl_2 (30 ml) was added dropwise a solution of $Me_3SiN{=}PPh_2CH_2PPh_2$ (3.02 g, 6.39 mmol), also in CH_2Cl_2 (25 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a light yellow solid. The product was washed with hexane (20 ml x 3) and then dried in vacuum. (Yield 2.92 g; 83%; light yellow powder). Anal. Calc'd for $C_{28}H_{22}N_4Cl_2P_2$: C, 61.44; H, 4.05; N, 10.24, Cl, 12.95. MS (EI, m/z): 546 (M+, 100 %). Found: C, 58.56; H, 4.41; N, 10.33, Cl, 9.59. ^1H NMR ($CDCl_3$): phenyl groups δ 7.40, 7.85 (m, 20H), PCH_2P methylene: δ 3.65 ppm (d, 2H, $^2J_{PH}$ = 16 Hz).

Synthesis of Bis(diphenyl [3,5-dichloro-2,4,6-s-triazine]-iminophosphino) methane (6-4):

To a solution of cyanuric chloride (0.333 g, 1.79 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of $Me_3SiN{=}PPh_2CH_2P(Ph)_2{=}NSiMe_3$ (0.500 g, 0.89 mmol), also in CH_2Cl_2 (25 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (20 ml x 3) and then dried in vacuum. (Yield 0.51 g; 72%; white powder). Anal. Calc'd for $C_{31}H_{22}N_8Cl_4P_2$: C, 52.42; H, 3.12; N, 15.77, Cl, 19.96. MS (EI, m/z): 710 (M+, 100 %). Found: C, 53.10; H, 3.10; N, 14.52, Cl, 19.74. ^1H NMR ($CDCl_3$): phenyl groups δ 7.60, 7.85 (m, 20H), PCH_2P methylene: δ 3.80 ppm (d, 2H, $^2J_{PH}$ = 16 Hz).

Synthesis of [(4,6-dichloro-2-(triphenylphosphinimino)-1,3,5-s-triazine){N, N}Rh(cod)](ClO_4) (6-5):

To a 100 ml Schlenk flask were added $[(cod)RhCl]_2$ (0.049 g, 0.10 mmol) and $AgClO_4$ (0.042 g, 0.20 mmol), and acetone (15 ml). The mixture was stirred for about 15 mins whereupon a light yellow solution and some white precipitate formed. This solution was filtered into a solution of **6-2** (0.073 g, 0.10 mmol), also in acetone (15 ml). The mixture was stirred for 1h. The solution was taken to near dryness, then hexane (10 ml) was added whereupon a yellow precipitate formed. The product was washed with hexane (15 ml x 2) and then dried in vacuum. (yield: 0.068 g; 51%; yellow powder). Anal. Calc'd for $C_{24}H_{25}N_4Cl_3O_4PRh$: C, 42.79; H, 3.74; N, 8.32; Cl, 15.79. MS (FAB): 573 (monocation). Found: C, 42.98; H, 3.77; N, 7.93; Cl, 15.38. ^1H NMR ($CDCl_3$): Phenyl groups: δ 7.55, 7.90 ppm (m, 10 H); Methyl group: δ 2.20 (m, 3H). cod groups: δ 4.20 ppm (broad, 4H, HC=), δ 2.60 ppm (broad, 4H), δ 1.75 ppm (broad, 4H, H_2C).

Synthesis of 4-chloro-6-(*p*-methylphenylamino)-2-(triphenylphosphinimino)-1,3,5-s-triazine (6-6):

To a solution of (**6-1**) (0.21 g, 0.50 mmol) in CH_2Cl_2 (30 ml) was added dropwise a solution of *p*-$MeC_6H_4NH_2$ (0.11 g, 1.0 mmol), also in CH_2Cl_2 (20 ml). The reaction mixture was stirred at room temperature for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (10 ml x 3) and then dried in vacuum to obtain the one-half dichloromethane solvate of **6-6**. (Yield 0.20 g; 74%; white powder). Anal. Calc'd for $C_{28}H_{23}N_5ClP \cdot 1/2CH_2Cl_2$: C, 63.58; H, 4.49; N, 13.01, Cl, 13.17. MS (EI, m/z): 494 (M+, 100 %). Found: C, 63.54; H, 4.98; N, 12.21, Cl, 12.51. ^1H NMR ($CDCl_3$): phenyl rings: δ 7.45, 7.60, 7.80 (m, 15H), -C_6H_4-: δ 6.65, 6.80 ppm (m, 4H), methyl group: δ 2.30 ppm (s, 3H).

Synthesis of 4,6-bis(phenylamino)-2-(triphenylphosphinimino)-1,3,5-s-triazine (6-7):

To a solution of (**6-1**) (0.43 g, 1.0 mmol) in CH_2Cl_2 (30 ml) was added dropwise a solution of $C_6H_5NH_2$ (0.36 ml, 4.0 mmol), also in CH_2Cl_2 (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (10 ml x 3) and then dried in vacuum to obtain the one-half dichloromethane solvate of **6-7**. (Yield 0.35 g; 60%; white powder). Anal. Calc'd for $C_{33}H_{27}N_6P \cdot 1/2CH_2Cl_2$: C, 69.25; H, 4.86; N, 14.46, Cl, 6.10. MS (EI, m/z): 537 (M+, 100 %). Found: C, 68.34; H, 4.92; N, 13.91, Cl, 6.31. ^1H NMR ($CDCl_3$): phenyl rings: δ 7.45, 7.60 (m, 15H), C_6H_5-: δ 6.70 ppm (m, 5H).

Synthesis of 4,6-bis(*p*-methylphenylamino)-2-(triphenylphosphinimino)-1,3,5-s-triazine (6-8):

To a solution of (**6-1**) (0.21 g, 0.50 mmol) in CH_2Cl_2 (30 ml) was added dropwise a solution of *p*-$MeC_6H_4NH_2$ (0.22 g, 2.0 mmol), also in CH_2Cl_2 (20 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a light yellow solid. The product was washed with hexane (10 ml x 3) and then dried in vacuum to obtain the 1:1 dichloromethane solvate of **6-8**. (Yield 0.26 g; 80%; light yellow powder). Anal. Calc'd for $C_{35}H_{31}N_6P{\cdot}CH_2Cl_2$: C, 66.36; H, 5.10; N, 12.90, Cl, 10.88. MS (EI, m/z): 566 (M+, 100 %). Found: C, 67.11; H, 5.67; N, 12.62, Cl, 9.32. ^1H NMR ($CDCl_3$): phenyl rings: δ 7.45, 7.60 (m, 15H), -C_6H_4-: δ 6.65, 6.80 ppm (m, 4H), methyl group: δ 2.30 ppm (s, 3H).

Synthesis of 4,6-dichloro-2-(3,5-dimethylpyrazole)-1,3,5-s-triazine (6-9):

To a solution of cyanuric chloride (1.02 g, 5.47 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of trimethylsilyl-3,5-dimethylpyrazole (0.92 g, 5.47 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum. (Yield 1.12 g; 84%; white powder). Anal. Calc'd for $C_8H_7N_5Cl_2$: C, 39.37; H, 2.89; N, 28.69, Cl, 29.05. MS (EI, m/z): 243 (M+, 100%). Found: C, 40.18; H, 2.71; N, 28.71, Cl, 28.56. ^1H NMR ($CDCl_3$): C-H: δ 6.12 ppm (s, 1H), methyl groups: δ 2.35 ppm (s, 3H), δ 2.70 ppm (s, 3H).

Synthesis of 6-chloro-2,4-bis(3,5-dimethylpyrazole)-1,3,5-s-triazine (6-10):

To a solution of cyanuric chloride (0.84 g, 4.52 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of trimethylsilyl-3,5-dimethylpyrazole (1.52 g, 9.05 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum. (Yield 1.15 g; 84%; white powder). Anal. Calc'd for $C_{13}H_{14}N_7Cl$: C, 51.40; H, 4.65; N, 32.28, Cl, 11.67. MS (EI, m/z): 303 (M+, 100 %). Found: C, 51.34; H, 4.71; N, 31.70, Cl, 12.26. ^{1}H NMR ($CDCl_3$): C-H: δ 6.10 ppm (s, 2H), methyl groups: δ 2.30 ppm (s, 6H), δ 2.75 ppm (s, 6H).

Synthesis of 2,4,6-tris(3,5-dimethylpyrazole)-1,3,5-s-triazine (6-11):

To a solution of cyanuric chloride (0.10 g, 0.54 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of trimethylsilyl-3,5-dimethylpyrazole (0.27 g, 1.61 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum to obtain the one-eighth dichloromethane solvate of **6-11**. (Yield 0.18 g; 89%; white powder). Anal. Calc'd for $C_{18}H_{21}N_9 \cdot 1/8CH_2Cl_2$: C, 58.20; H, 5.73; N, 33.70, Cl, 2.37. MS (EI, m/z): 363 (M+, 100 %). Found: C, 58.28; H, 5.72; N, 34.65, Cl, 2.85. ^{1}H NMR ($CDCl_3$): C-H: δ 6.12 ppm (s, 3H), methyl groups: δ 2.35 ppm (s, 9H), δ 2.80 ppm (s, 9H).

Synthesis of 6-chloro-4-(3,5-dimethylpyrazole)-2-(triphenylphosphinimino)-1,3,5-s-triazine (6-12):

To a solution of (**6-9**) (0.24 g, 1.00 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of $Ph_3P=N\text{-}SiMe_3$ (0.35 g, 1.00 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum to obtain the one-half dichloromethane solvate of **6-12**. (Yield 0.45 g; 85%; white powder). Anal. Calc'd for $C_{26}H_{22}N_6ClP\cdot 1/2CH_2Cl_2$: C, 60.35; H, 4.40; N, 15.93, Cl, 13.44. MS (EI, m/z): 485 (M+, 100 %). Found: C, 61.15; H, 4.54; N, 15.82, Cl, 13.52. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.60, 7.85 ppm (m, 15H), C-H: δ 5.92 ppm (s, 1H), methyl groups: δ 2.25 ppm (s, 3H), δ 2.35 ppm (s, 3H).

Synthesis of 6-chloro-4-(3,5-dimethylpyrazole)-2-($N=PPh_2CH_2PPh_2$)-1,3,5-s-triazine (6-13):

To a solution of (**6-9**) (0.23 g, 0.93 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of $P(Ph)_2CH_2P(Ph)_2P=N\text{-}SiMe_3$ (0.44 g, 0.93 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum to obtain the one-eighth dichloromethane solvate of **6-13**. (Yield 0.45 g; 80%; white powder). Anal. Calc'd for $C_{33}H_{29}N_6ClP_2\cdot 1/8CH_2Cl_2$: C, 64.42; H, 4.77; N, 13.61, Cl, 7.18. MS (EI, m/z): 607 (M+, 100 %). Found: C, 64.42; H, 5.38; N, 13.62, Cl, 7.66. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.25, 7.45 7.90 ppm (m, 20H), PCH_2P methylene: δ 4.05 ppm (d, 2H, $^2J_{PH}$ = 15 Hz), C-H: δ 6.00 ppm (s, 1H), methyl groups: δ 2.30 ppm (s, 3H), δ 2.65 ppm (s, 3H).

Synthesis of 4,6-(3,5-dimethylpyrazole)$_2$-2-(triphenylphosphinimino)-1,3,5-s-triazine (6-14):

To a solution of (**6-10**) (0.30 g, 1.00 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of Ph_3P=N-$SiMe_3$ (0.35 g, 1.00 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum. (Yield 0.48 g; 88%; white powder). Anal. Calc'd for $C_{31}H_{29}N_8P$: C, 68.37; H, 5.37; N, 20.58. MS (EI, m/z): 545 (M+, 100 %). Found: C, 59.61; H, 4.89; N, 5.93, Cl, 17.30. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.60, 7.85 ppm (m, 15H), C-H: δ 5.90 ppm (s, 1H), methyl groups: δ 2.05 ppm (s, 3H), δ 2.60 ppm (s, 3H).

Synthesis of 4,6-bis(3,5-dimethylpyrazole)-2-(N=$PPh_2CH_2PPh_2$)-1,3,5-s-triazine (6-15):

To a solution of (**6-10**) (0.30 g, 1.00 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of $P(Ph)_2CH_2P(Ph)_2P$=N-$SiMe_3$ (0.47 g, 1.00 mmol), also in CH_2Cl_2 (15 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (15 ml x 3) and then dried in vacuum. (Yield 0.55 g; 82%; white powder). Anal. Calc'd for $C_{38}H_{36}N_8P_2$: C, 68.46; H, 5.44; N, 16.81. MS (EI, m/z): 667 (M+, 100 %). Found: C, 67.03; H, 5.33; N, 3.63, Cl, 10.45. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.30, 7.80 ppm (m, 20H), PCH_2P methylene: δ 3.85 ppm (d, 2H, $^2J_{PH}$ = 16 Hz), C-H: δ 6.75 ppm (s, 2H), methyl groups: δ 2.25 ppm (s, 3H), δ 2.30 ppm (s, 3H), δ 2.35 ppm (s, 3H), δ 2.48 ppm (s, 3H).

Synthesis of 5-chloro-2,6-difluoro-4-(triphenylphosphinimino)-pyrimidine (6-16):

To a solution of 5-chloro-2,4,6-trifluoro-pyrimidine (0.34 g, 1.98 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of $Me_3SiN{=}PPh_3$ (0.69 g, 1.98 mmol), also in CH_2Cl_2 (25 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (20 ml x 3) and then dried in vacuum. (Yield 0.66 g; 78%; white powder). Anal. Calc'd for $C_{22}H_{15}N_3F_2ClP$: C, 62.06; H, 3.55; N, 9.87, Cl, 8.33. MS (EI, m/z): 426 (M+, 100%). Found: C, 61.73; H, 3.12; N, 9.74, Cl, 8.89. ^{19}F NMR ($CDCl_3$): δ (F_1(between two nitrogen) -69.42 ppm (d, 1F, $^5J_{PF}$ = 2.90 Hz), δ (F_2) -52.84 ppm (s, 1F). ^1H NMR ($CDCl_3$): phenyl groups: δ 7.55, 7.85 (m, 15H).

Synthesis of 2,5,6-trichloro-4-(triphenylphosphinimino)-pyrimidine (6-17):

To a solution of 2,4,5,6-tetrachloro-pyrimidine (0.45 g, 2.00 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of $Me_3SiN{=}PPh_3$ (0.70 g, 2.00 mmol), also in CH_2Cl_2 (25 ml). The reaction mixture was refluxed for 12h before the solvent was removed *in vacuo* to leave a colorless solid. The product was washed with hexane (20 ml x 3) and then dried in vacuum. (Yield 0.66 g; 78%; white powder). Anal. Calc'd for $C_{22}H_{15}N_3Cl_3P$: C, 57.60; H, 3.30; N, 9.16, Cl, 23.19. MS (EI, m/z): 458 (M+, 100%). Found: C, 57.50; H, 3.91; N, 6.09, Cl, 18.01. ^1H NMR ($CDCl_3$): phenyl groups: δ 7.50, 7.60, 7.85 (m, 15H).

Electrochemistry of *p*-benzoquinone derivatives

The working electrode was a small (about 1 mm diameter) Pt bead sealed in soft glass. A coiled Pt wire (about 15 cm in length) was used as the auxiliary electrode. The compartment for the Ag/AgCl quasi-reference electrode was separated from the working electrode compartment by a fine frit. The support electrode was [n-Bu_4N]BF_4. The solvent (dichloromethane, Spectrograde, BDH) was degassed and then dried over alumina (ICN Biomedical, neutral, W200 Super 1). The working electrode was cleaned by placing the electrode tip over boiling HNO_3 (reagent grade) for 0.5h, rinsing with distilled water (2 L), and then soaking it in a saturated ferrous ammonium sulphate solution (made up in 1 M H_2SO_4) for 0.5h. Finally, it was rinsed with distilled water (2 L) and reagent acetone (1 L), and then dried with a hot air gun immediately before use.

An electrochemical cell was constructed to provide a small volume (c.a. 10 ml) inert gas blanketted environment for the measurements. Three electrodes were introduced through a sealed glass cap extending to the base of the tube where they projected into the solution volume. A gas inlet and a side-arm was connected to the cell, the later was provided with a bent sample tube to hold the solid sample ready for addition. The procedure was carried out as follows: First, the sample was put in the sample side-arm tube, the solvent was added to the cell and a blank measurement was done. Then the sample tube was turned to drop the sample into the solvent. The sample was allowed to sissolve completely, and then the CV scan of the solution determined.

The potential was supplied by a EG&G Model 175 Universal Programmer, and the resulting cyclic voltammograms were recorded using a Hewlett Packard RE 0074 X-Y recorder. The solutions employed during cyclic voltammetry were typically (5-7) x 10^{-4} M in organometallic complex and 0.1 M in [n-Bu_4N]BF_4. These experiments were carried out at ambient temperatures (about 23 °C). The formal oxidation or reduction potential, $E^{o\prime}$, for reversible couples is defined as the average of the anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) peak potentials. The separation of the cathodic and anodic potentials is ΔE, $| E_{p,c} - E_{p,a} |$. The cathodic to anodic peak current ratio is defined as $i_{p,c}/i_{p,a}$.[170] The oxidation of ferrocene is reported to be highly reversible in many solvents[171] and was used as an internal reference (under our experimental conditions, $E^{o\prime} = + 0.47$ V *vs* Ag/AgCl, $i_{p,c}/i_{p,a} = 1.0$, $\Delta E = 100$ mV).[168] A scan rate of 0.1 V s^{-1} was used for all the compounds measured. The ratio $i_{p,c}/i_{p,a}$ was used to establish chemical reversibility for the compounds studied.

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